# Arylthianthrenium salts for triplet energy transfer catalysis

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Sigma bond cleavage through electronically excited states allows synthetically useful transformations with two radical species. Direct excitation of simple aryl halides to form both aryl and halogen radicals necessitates UV-C light, so undesired side reactions are often observed, and specific equipment is required. Moreover, only aryl halides with extended  $\pi$  systems and comparatively low triplet energy are applicable to synthetically useful energy transfer catalysis with visible light. Here we show the conceptual advantages of arylthianthrenium salts (ArTTs) for energy transfer catalysis with visible light in high quantum yield as compared to conventional aryl(pseudo)halides, and their utility in arylation reactions of ethylene. The fundamental advance is enabled by the low triplet energy of ArTTs that may originate in large part from the electronic interplay between the distinct sulfur atoms in the tricyclic thianthrene scaffold, which is neither accessible in simple (pseudo)halides nor other conventional sulfonium salts.



**Fig. 1 Reactivity of aryl electrophiles in ground and excited states. a**, fundamental reactivity for aryl electrophiles in the ground state. Ar, aryl group; Nu, nucleophile; M, transition metal; X, (pseudo)halide; EDA, electron donor-acceptor. **b**, homolytic cleavage of C–X bonds in aryl halides from excited singlet state obtained under UV-C radiation. UV-C, UltraViolet C. **c**, mesolytic cleavage of ArTTs through SET and homolytic cleavage of ArTTs through triplet EnT with visible light. SET, single electron transfer; EnT, energy transfer; TXO, thioxanthone.

Aryl(pseudo)halides are versatile electrophiles in organic synthesis owing to the broad reactivity of their polar C–X bond in their ground state (Fig. 1a)<sup>1,2</sup>. Electronically excited aryl halides can undergo homolysis of the C–X bond to form two synthetically useful radical species, a reactivity that is usually unattainable from the ground state on account of the large bond dissociation energy (BDE) of the C–X bonds, for example around 84 kcal·mol<sup>-1</sup> for aryl bromides<sup>3</sup>. Yet, aryl halides typically do not absorb in

the visible spectrum, so UV light, often in the UV-C spectrum (< 280 nm), is required for their excitation, which delivers over 102 kcal·mol<sup>-1</sup> of energy, capable of cleaving many organic bonds, including C-C (~83 kcal·mol<sup>-1</sup>) and C-H bonds (~100 kcal·mol<sup>-1</sup>) (Fig. 1b)<sup>4</sup>. Visible light provides photons with less than 75 kcal·mol<sup>-1</sup> energy, which allows most organic covalent bonds to remain intact. Additionally, visible light is safer, more accessible, and does not require special equipment, such as quartz glassware. However, simple aryl (pseudo)halides must typically be excited through direct excitation to a singlet state with UV-C light. Electronic excitation through triplet energy transfer (EnT) processes from an excited sensitizer are promising but have not been applied to simple any halides with visible light<sup>5-8</sup>. Because triplet energy  $(E_T)$ and spin multiplicity are transferred via concurrent electron exchange between an excited photosensitizer donor and the substrate acceptor, the excited high-energy singlet state of the substrate is circumvented. Nevertheless, sensitization of simple aryl halides requires higher triplet energy than is obtainable from photosensitizers with visible light absorption, which generally exhibit triplet energies of less than 66 kcal·mol<sup>-1</sup>.<sup>6-8</sup> Only special aryl halides with an appropriate electronic structure have a sufficiently low triplet energy for successful excitation, for example, through extended  $\pi$  systems<sup>9</sup>. Aryl halides with highly conjugated or fused aryl systems, such as biphenyl and naphthyl halides, have low enough triplet energies  $(60-64 \text{ kcal} \cdot \text{mol}^{-1})^9$  and can be used in energy transfer catalysis with visible light<sup>10,11</sup>. For simple aryl halides, less than 280 nm UV light and quartz glassware must be used<sup>10</sup>. High-power LEDs with high electricity-to-light conversion efficiencies are only available with wavelengths starting from about 365 nm<sup>12</sup>. Other synthetically useful, colorless molecules with a triplet energy of less than 66 kcal·mol<sup>-1</sup> include, for example, styrene-derived substrates<sup>6-8</sup>, disulfides<sup>13</sup>, benzophenone-based oxime carbonates<sup>14</sup>, fused arenes<sup>15</sup>,  $\alpha$ -ketoesters<sup>16</sup>, N–N pyridinium ylides<sup>17</sup>, and naphthyl ketones<sup>18</sup>. Aryldiazonium and – iodonium compounds primarily function as electron acceptors rather than energy acceptors as a result of their high reduction potentials that can be rationalized, in part, by their positive charge, which favors capturing an electron instead of accepting energy from an excited photosensitizer<sup>19</sup>. Although both single electron transfer (SET) and EnT can generate synthetically useful aryl radicals from aryl(pseudo)halides, SET produces negatively charged (pseudo)halides after mesolytic cleavage, whereas EnT generates

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neutral (pseudo)halogen radicals after homolytic cleavage, and thereby provides a conceptually different reactivity mode that can be exploited for distinct reaction chemistry beyond what is possible with SET chemistry<sup>20</sup>. So far, a general platform for visible light-induced homolysis of the C–X bond in aryl electrophiles is lacking, both in terms of direct excitation and triplet energy transfer, and synthetically useful transformations based on excited aryl electrophiles still rely on the use of harmful UV light<sup>4,21</sup>. ArTTs have been shown to participate in various mechanisms, for example, transition metal catalysis<sup>22</sup>, photoredox catalysis<sup>23</sup>, direct excitation with 254 nm light<sup>21</sup>, and charge transfer processes<sup>24</sup> but not energy transfer processes. Herein, we analyze the electronic structure of arylthianthrenium salts, describe their differences to aryl halides and other aryl-based positively charged pseudohalides, such as aryldiazonium salts, and show that arylthianthrenium salts undergo productive energy transfer to enable chemistry, which has not been accomplished with any other aryl (pseudo)halides (Fig. 1c).

Manipulation of HOMO/LUMO energy states and triplet energy with electron donor and acceptor substituents to obtain bipolar molecules has been widely employed in the development of phosphorescent organic light-emitting diodes (PhOLEDs)<sup>25</sup> and organic photocatalysts<sup>26</sup>. A priori, triplet energies cannot be derived from HOMO-LUMO gaps, yet, it is acknowledged that triplet energies are correlated with the degree of conjugation in molecules<sup>6,9</sup>, and so are HOMO-LUMO gaps. Arylthianthrenium salts<sup>22</sup> possess a positively charged, therefore strongly electron-accepting, sulfur atom, and a neutral, electron-donating sulfur atom, the combination of which may result in a lower HOMO-LUMO gap and in a lower triplet energy. We speculate that the lower triplet energy of ArTTs may be determined by the dipolar structure of the thianthrenium substituent itself, and not primarily influenced by the arene, and should therefore render ArTTs with varying aryls promising candidates for energy transfer catalysis with visible light. Furthermore, cationic ArTTs are less likely to engage in SET with commonly used photosensitizers when compared to other aryl-based cations such as phenyl diazonium (-0.1 V vs SCE) and -iodonium salts (-0.8 V vs SCE) due to their more negative reduction potential (-1.5 V vs SCE)<sup>23</sup>. Energy transfer to arylthianthrenium salts would result in an excited triplet state and the formation of aryl radicals and the

persistent thianthrenium radical cation (TT<sup>\*\*</sup>) upon homolysis, which is distinct from single electron transfer (SET) and electron donor-acceptor (EDA) complex pathways that form neutral thianthrene after mesolytic cleavage. The conceptually different reactivity mode of EnT offers distinct opportunities for reaction chemistry beyond what SET or EDA complex pathways have enabled, and may result in significantly higher quantum yields and thereby energy efficiency. As a proof of concept, we demonstrate the 1,2-arylfunctionalization reactions of ethylene<sup>27</sup>, a transformation currently inaccessible from other activation modes and other aryl(pseudo)halides with visible light<sup>28</sup>.

# **Results and discussion**

### Reaction development and mechanistic investigations



**Fig. 2 Development and application of arylthianthrenium salts for triplet energy transfer catalysis. a**, evaluation of different photocatalysts in the 1,2-arylfunctionalization reactions of ethylene with arylthianthrenium salt **1**. Triplet energies (E<sub>T</sub>) and reduction potentials (E vs SCE) are literature values<sup>29,30</sup>. <sup>a</sup>20 mol% catalyst loading, 20 min. OTf, triflate; Mes-Acr, 9-mesityl-10-methylacridinium ion; bpy, 2,2'bipyridyl; ppy, 2-phenylpyridyl; 3CzClIPN, 2,4,6-tri(9*H*-carbazol-9-yl)-5-chloroisophthalonitrile; n/a, not available. **b**, evaluation of different aryl (pseudo)halides with thioxanthone as photosensitizer. **c**, correlation between reaction rates and triplet energy of different 2-substituted TXO photosensitizers. Triplet energies are calculated values (Supplementary Tab. S13). **d**, proposed mechanism.

To probe our hypothesis that ArTTs could act as energy acceptor and undergo homolytic C-S bond cleavage with visible light, we exposed arylthianthrenium salt 1 to 390 nm LED irradiation in the presence of various photocatalysts under 1 atmosphere of ethylene gas. Efficiency of the reaction correlated with the triplet energy of the photosensitizer and not with the reduction potentials of the excited state (Fig. 2a), which points towards an EnT process as opposed to an SET process. By employing the commonly used thioxanthone (TXO) photosensitizer, with a triplet energy of 65.5 kcal·mol<sup>-1</sup>,<sup>31</sup> the desired arylethyl thianthrenium salt 2 was formed in 82% yield within 2 minutes at -78 °C. At room temperature, the solubility of ethylene in acetone is significantly lower, which leads to the formation of hydrodefunctionalized byproducts via hydrogen abstraction by aryl radicals. Longer reaction time results in lower yield, presumably due to unproductive energy transfer to the product alkyl thianthrenium salt. The catalyst loading can be as low as 1.0 mol%, which is uncommon when utilizing TXO as a photocatalyst because of the occurrence of undesired hydrogen atom abstraction with excited TXO<sup>32</sup>. The low catalyst loading can be attributed to either the absence of a proper hydridic hydrogen atom in the reaction or efficient energy transfer facilitated by significant overlap between excited TXO and thianthrenium salts (vide infra). Other photosensitizers with triplet energies below 62.8 kcal·mol<sup>-1</sup> all exhibit less than 2% conversion. Benzophenone, a photosensitizer with a higher triplet energy of 69.3 kcal·mol<sup>-1</sup>,<sup>29</sup> requires a catalyst loading of 20 mol% and a prolonged reaction time of 20 min to afford a similar yield, likely due to the low absorption coefficient at 390 nm. Phenyl chloride (1a), bromide (1c), iodide (1e), and triflate (1g) do not show reactivity under the same conditions (Fig. 2b), likely owing to their high triplet energy ( $\sim$ 82 kcal·mol<sup>-1</sup>)<sup>9</sup>, which renders the triplet state energetically inaccessible with visible light sensitization. Although biphenyl halides (1b, 1d, 1f) have an energetically reachable triplet energy of around 63 kcal·mol<sup>-1,9</sup> they do not participate in an efficient reaction, possibly on account of prohibitively high BDEs of the C-X bonds<sup>33</sup>, or less efficient energy transfer owing to lower overlap with the excited sensitizer compared to thianthrenium salts (vide infra). Other phenyl sulfonium salts, like triphenylsulfonium<sup>34</sup> and 5-phenyldibenzothiophenium salts<sup>35</sup>, show negligible reactivity, possibly as a result of the instability of the diphenyl sulfide- or dibenzothiophene radical cation<sup>36</sup>, insufficient overlap,

or both. Although the phenoxathiin radical cation is also persistent,<sup>36</sup> its corresponding salt is less efficient than arylthianthreniums.

Diaryl ketones are often employed as triplet photosensitizers rather than photoredox catalysts, primarily owing to their high triplet energy, notable efficiencies in intersystem crossing (typically  $\Phi_{ISC} > 0.90$ ), and long-lived triplet excited states of approximately 50 µs<sup>29</sup>. Use of several 2-substituted TXOs with different triplet energy and reduction potentials illustrates a positive correlation between triplet state energy and reaction rates, which is consistent with the involvement of an EnT pathway (Fig. 2c). The absence of a positive correlation between reaction rates and redox potentials of TXOs in both ground and excited states renders an SET pathway less likely (Supplementary Fig. S8). Furthermore, electronically excited TXO (-1.11 V vs SCE) and benzophenone (-0.61 V vs SCE)<sup>29</sup> exhibit insufficient reduction potentials for single electron reduction of ArTTs ( $\sim -1.5$  V vs SCE)<sup>23</sup>. The lack of interaction between ArTTs and TXO in the ground state, as observed from UV-vis studies, precludes the formation of an electron donoracceptor (EDA) complex (Supplementary Fig. S4)<sup>24</sup>. Triplet quenchers, such as anthracene and cyclooctatetraene, decelerate or even inhibit the reaction, which is also consistent with an EnT pathway (Supplementary Tab. S10). A quantum yield value of  $\Phi = 0.1$  is below 1 and consistent with a pathway that does not proceed via a chain mechanism. The observed positive but relatively small Hammett  $\rho$  value of 1.8 (Supplementary Fig. S10) aligns with the reduction of positive charge on the aromatic ring in the transition state. The bond dissociation energy (BDE) of the exocyclic C-S bond in PhTT<sup>+</sup> has been computed to be only at 64.2 kcal·mol<sup>-1</sup>, slightly lower than its triplet state energy, which implies the prospect for synthetically useful homolytic cleavage following sensitization.



Fig. 3 Mechanistic studies through photophysical analysis. **a**, phosphorescence measurements of PhTT<sup>+</sup> and **1** at 77 K. **b**, Stern-Volmer analysis of <sup>3</sup>TXO quenching by PhTT<sup>+</sup> and **1**. **c**, kinetic traces of <sup>3</sup>TXO quenching (top) and isolated TT<sup>++</sup> formation and decay (bottom). **d**, transient absorption spectra of 50  $\mu$ M TXO and 1mM PhTT<sup>+</sup> after 50 ns (purple) and 50  $\mu$ s (cyan) and comparison of direct and sensitized bond homolysis. Inset: absorption spectrum of thianthrenium radical cation (as tetrafluoroborate).

We carried out detailed laser flash photolysis experiments: The 77 K phosphorescence spectra obtained upon pulsed excitation for PhTT<sup>+</sup> and ArTT<sup>+</sup> (1) give experimental triplet energies (Fig. 3a) that are in agreement with computed E<sub>T</sub> values (see below) and comparable to that of <sup>3</sup>TXO. In line with an almost isoenergetic (PhTT<sup>+</sup>) and a slightly thermodynamically uphill (ArTT<sup>+,</sup> 1) EnT process, we measured quenching rate constants that are slower than the diffusion limit by about two orders of magnitude (Fig. 3b). Transient absorption studies revealed that upon <sup>3</sup>TXO quenching a single intermediate (Fig. 3c) with a characteristic spectrum in the visible range is formed, which we could unambiguously assigned to TT<sup>++</sup> (Fig. 3d)<sup>37</sup>. TXO-derived products that would result from a photoinduced SET can be excluded<sup>38</sup>, substantiating the anticipated EnT process followed by homolytic bond cleavage. In contrast, SET is the primary quenching mechanism with Ir(dFppy)<sub>3</sub> (Supplementary Fig. S1). Quantitative laser experiments with the excitation wavelength 355 nm allowed us to compare the quantum efficiency of TT<sup>++</sup> and aryl radicals (that do not absorb in our detection range) generation upon direct UV excitation and sensitization

at 20°C. Based on our results, the EnT approach is inherently more efficient by as much as a factor of 18, highlighting another advantage of the strategy presented herein. These mechanistic studies explain the impressively short reaction times and considerable overall quantum yield observed at lower temperatures. We believe that highly efficient photocatalytic reaction protocols as presented herein are required for the development of photoreactions on a larger scale and industrially scalable photoreactions, which is why our paper represents a conceptual breakthrough.

Based on our collective experimental findings, we propose an operative mechanism as shown in Fig. 2d, in which electronically excited TXO sensitizes ArTTs through energy transfer to yield triplet-excited ArTTs that undergoes rapid homolysis of the labile C–S bond to produce an aryl radical and persistent TT<sup>\*\*</sup>. The aryl radical adds to ethylene to form a highly reactive primary homobenzyl radical, which is then captured by TT<sup>\*\*</sup> to afford the product. Because TT<sup>\*\*</sup> is persistent, as opposed to radicals derived from other aryl(pseudo)halides, productive radical recombination is not challenged by side reactions resulting from TT<sup>\*\*</sup>, as could be expected from other radicals, such as hydrogen atom abstraction from chlorine or bromine radicals<sup>39</sup>, and decomposition of diphenyl sulfide-<sup>34</sup> or iodobenzene radical cations<sup>40</sup>. The observation of crossover products in a radical scrambling experiment (Supplementary Fig. S9) using two different salts, Ar<sup>1</sup>TT<sup>+</sup> and Ar<sup>2</sup>TFT<sup>+</sup>, indicates that radicals escape from the solvent cage precedes the C–S bond formation process.

#### Computational study of ground and triplet states of aryl(pseudo)halides



### Fig. 4 Computational study of aryl(pseudo)halides and Dexter energy transfer mechanism. a,

comparison of frontier molecular orbitals energy of different aryl(pseudo)halides. FMOs, frontier molecular orbitals; Ph, phenyl; OTf, triflate; Ph<sub>3</sub>S<sup>+</sup>, triphenylsulfonium; PhPT<sup>+</sup>, 10phenylphenoxathiinium; PhDBT<sup>+</sup>, 5-phenyldibenzothiophenium; Ph<sub>2</sub>I<sup>+</sup>, diphenyl iodonium salt; PhN<sub>2</sub><sup>+</sup>, phenyl diazonium salt. **b**, relationship between triplet energy of aryl(pseudo)halides p-Y-C<sub>6</sub>H<sub>4</sub>X and conjugation extent of their parent C<sub>6</sub>H<sub>5</sub>Y. Triplet energies for p-Y-C<sub>6</sub>H<sub>4</sub>Cl and p-Y-C<sub>6</sub>H<sub>4</sub>Br are literature values<sup>16</sup>. Ac, acetyl group; E<sub>T</sub>, triplet energy; X, (pseudo)halide; Y, substituent. **c**, Dexter energy transfer mechanism and possible Dexter energy transfer model.

Density Functional Theory (DFT) calculations were conducted to elucidate the conceptual difference between ArTTs and other aryl(pseudo)halides in energy transfer chemistry. Although the bent geometry of

the thianthrenium framework limits extensive conjugation potential<sup>22</sup>, the calculation results predict that PhTT<sup>+</sup> exhibits a narrower HOMO-LUMO gap in comparison to phenyl halides and other structurally similar phenyl sulfonium salts (Fig. 4a). As for other positively charged aryl-substituted salts, the LUMO of PhTT<sup>+</sup> is significantly lower than for neutral aryl halides, yet its HOMO is comparatively high when compared to the other cations, possibly a result of the electron-rich neutral sulfur atom, which leads to a smaller HOMO-LUMO gap. PhTT<sup>+</sup> is computed to have a triplet energy of 65.5 kcal·mol<sup>-1</sup> that is in agreement with the experimental value, significantly lower than that of corresponding phenyl halides (~82 kcal·mol<sup>-1</sup>)<sup>9</sup> and triphenyl sulfonium salt ( $\sim$ 75 kcal·mol<sup>-1</sup>)<sup>34</sup>. While phenyl diazonium and -iodonium salts also possess low triplet energies of 61.8 kcal·mol<sup>-1</sup> (Supplementary Tab. S14) and 64.3 kcal·mol<sup>-1</sup> respectively<sup>40-42</sup>, their lower LUMO energy levels likely result in higher electron affinity and faster electron transfer than for ArTTs<sup>19</sup>. DFT calculations also indicate that the frontier molecular orbitals of phenyl halides are mainly located within the aromatic  $\pi$  system, while the TT framework contributes significantly to the frontier molecular orbitals of ArTTs (Supplementary Tab. S14). Likewise, the triplet state energy of ArTTs appears to be governed by the TT substituent, which remains similar between 60–66 kcal·mol<sup>-1</sup>, largely independent of the aryl substituent (Fig. 4b). In contrast, the triplet energy of aryl halides is significantly influenced by substituents, and exhibits a stronger correlation with the HOMO-LUMO gaps of their parent arenes.

The reaction is rapid and reaches full conversion within 2 minutes at a catalyst loading of just 1.0 mol% and a reaction temperature of -78 °C. We propose that the geometry of the electronic overlap between excited TXO and ArTTs plays an important role as well: In a Dexter energy transfer process, simultaneous exchange of electrons between excited photosensitizer and substrate result in energy transfer (Fig. 4c)<sup>43</sup>. The frontier molecular orbitals ( $\alpha$ -HOMO and  $\beta$ -LUMO) of the excited TXO are predominantly situated on the carbon of the carbonyl group and the sulfur atom, respectively, while those of the ground state PhTT<sup>+</sup> are primarily located on the neutral and positively charged sulfur atoms, respectively. Given the analogous tricyclic fused ring system of TXO and thianthrenium, the spatial alignment of the frontier orbitals of excited TXO and ground state PhTT<sup>+</sup> coincides. In view of the significant impact of orbital interactions on energy transfer rates<sup>43</sup>, the interplay between thianthrenium and TXO may result in rapid energy transfer. Such a hypothesis would also provide additional insight into why arylthianthreniums react more favorably, even than those special aryl pseudohalides (Fig. 2b) with appropriate triplet energy, and why other well-established photosensitizers such as benzophenone are significantly less efficient. Such fortuitous energy transfer, based on the thianthrenium structure, is yet another example of how thianthrene-chemistry can elicit desired chemical reactivity beyond what is currently possible with conventional (pseudo)halides.

### Table 1 Substrate scope<sup>a</sup>



<sup>a</sup>Reaction conditions: arylthianthrenium salt (0.20 mmol), ethylene (1 atm), and TXO in acetone (c = 0.50 mM, 4.0 mL, 2.0 µmol, 1.0 mol%) at -78 °C under 40 W 390 nm LED for 2–15 min. Subsequently, base and nucleophile were added, and the reaction mixture was stirred for 12 hours. Refer to the supporting information for experimental details for each substrate. <sup>b</sup>Tetrabutylammonium bormide (TBAB, 77 mg,

0.24 mmol, 1.2 equiv) was added in the first step and allowed to react at -94 °C for 10 min. °Tetrabutylammonium chloride (TBACl) was used. <sup>d</sup>DBU was used. <sup>e</sup>KI was used. <sup>f</sup>Water was used at 55 °C. <sup>g</sup>Triethylamine trihydrofluoride was used at 55 °C. <sup>h</sup>Anhydrous methanol was used as solvent in the second step at 55 °C. <sup>i</sup>NaBr was used.

### Substrate scope

ArTTs with different substituents display comparable triplet energy between 60–65 kcal·mol<sup>-1</sup>, lower than the triplet energy of TXO, which suggests a broad theoretical scope of aryl electrophiles for productive and chemoselective sensitization with visible light. As shown in Table 1, a variety of ArTTs bearing ortho-, meta-, and para-substituted aryls, and electron-rich, -neutral, and -poor aryls, as well as mono-, di-, and tri-substituted aryls, are tolerated. In our prior research utilizing aryl halides as energy acceptors, only substrates featuring highly conjugated biphenyl and naphthyl frameworks are effective with visible light, and 280 nm UV-C light is necessary when employing simple aryl halides<sup>10</sup>. Here, no such limitation was observed and visible light could be used for all examples. Various functional groups, heteroaromatic compounds, and complex molecules are well-tolerated. Given the higher triplet energy and lower rate of energy transfer to aryl halides compared to ArTTs, halides (7, 22, 25) remain untouched and can be potentially utilized in subsequent transformations. The large functional group tolerance may also be explained by a chemoselective Dexter energy transfer that is fastest between the TXO photosensitizer and the thianthrenium group based on their structural and electronic similarity, and leave other functional groups, potentially sensitive to energy transfer and hydrogen atom transfer, untouched. The main side products include hydrodefunctionalization, which can be reduced by further decreasing the reaction temperature to -94 °C, thereby increasing the solubility of ethylene, and the Minisci byproduct, which can be minimized by carefully controlling the reaction time or suppressed by adding a bromide nucleophile to capture the alkyl thianthrenium salt (Supplementary Scheme S1).

The resulting primary arylethyl thianthrenium salts serve as effective alkyl electrophiles for subsequent transformations<sup>44,45</sup>. By employing amines as nucleophiles in the same pot, a useful yet otherwise 15

challenging three-component aminoarylation reaction involving aryl electrophiles, alkenes, and amines was achieved (Table 1)<sup>46</sup>. In previous studies with different approaches, aminoarylation of alkenes showed a wide range of alkenes, yet the scope of amines was limited to azide and nitriles<sup>47-49</sup>. In our study, both the scope of amines and the tolerance towards functional groups are extensive. A wide range of amines, including cyclic and acyclic, primary, secondary, and tertiary, along with aliphatic and aromatic amines, all demonstrate excellent compatibility. A variety of valuable  $\beta$ -arylethylamines are synthesized, which are privileged pharmacophores found in a range of biologically active natural products and pharmaceuticals, particularly in molecules that act on the central nervous system<sup>47,48</sup>. Oxygen-, sulfur-, and chloride-based nucleophiles allow for the direct synthesis of  $\beta$ -arylethyl ethers, -thioethers, and chlorides, all of which are found in various pharmaceuticals and bioactive molecules. Nucleophiles based on carbon, phosphine, other halides, and selenium are all compatible, which demonstrates the versatile ability of neutral thianthrene to function as excellent leaving group. The wide variety of aromatic components and nucleophiles allows for fragment coupling through a  $-CH_2CH_2$ -linker (27). Nucleophiles with high basicity, such as fluoride, and carbon nucleophiles like cyanide, malonates or acetylides, resulted in low yield (< 40%) because of competing elimination reactions, a side reactivity also observed with other nucleophiles except halides (Cl, Br, I), sulfur, and selenium-based ones. The elimination side reaction can be mitigated by converting alkylthianthrenium salts to alkyl bromides in situ before adding the nucleophile, as uncharged alkyl bromides are less prone to elimination. When a nonnucleophilic base, such as DBU was employed, elimination was observed exclusively, and vinylated arene (8) was obtained.

Substituted alkenes can be effectively utilized in the presence of bromide nucleophiles to capture alkyl thianthrenium salts, affording alkyl bromides in 53–81% yields. Unactivated monosubstituted alkenes, such as propene, can be applied and potentially used to synthesize drug-related amphetamine candidates via amination. Additionally, 1,1- and 1,2-disubstituted alkenes like 2-methylpentene, 2-methylacrylate, and fumarate also work well, providing secondary and tertiary alkyl bromides that otherwise difficult to synthesize from other methods. Styrene and Michael acceptors, such as acrylonitrile, acrylamide, vinyl 16

sulfone, and vinyl phosphonate, also perform effectively, yielding activated alkyl bromides suitable for further transformations.



### Table 2 Substrate scope of alkenes

<sup>a</sup>Reaction conditions: arylthianthrenium salt (0.20 mmol), alkenes (0.60 mmol, 3.0 equiv), TBAB (77 mg, 0.24 mmol, 1.2 equiv), and TXO in MeCN (c = 0.50 mM, 4.0 mL, 2.0 µmol, 1.0 mol%) at -20 °C under 40 W 390 nm LED for 5 min. <sup>b</sup>10 equiv alkene used. <sup>c</sup>15 min.

## Conclusions

We have demonstrated the conceptual advantage of ArTTs to enable visible light-mediated triplet energy transfer catalysis. Our study highlights the pivotal role of the two sulfur atoms in reducing the HOMO-LUMO gap and triplet energy of ArTTs. In view of the small influence of the aryl group, various ArTTs exhibit similar triplet energy. The large structural and electronic overlap between the excited TXO and 17

thianthrenium framework facilitates rapid visible light-driven energy transfer with much higher inherent quantum yields compared to direct UV excitation<sup>50</sup>. By employing ArTTs as energy acceptors, we have presented synthetically valuable arylethylation reactions of amines, alcohols and other nucleophiles. Further exploration of thianthrenium salts as acceptor for triplet energy transfer catalysis may unveil additional useful reaction chemistry.

### Methods

General procedure. To a 5-mL Schlenk tube containing a Teflon-coated magnetic stirring bar were added arylthianthrenium salt (0.200 mmol, 1.00 equiv) and thioxanthone in acetone (c = 0.50 mM, 4.0 mL, 2.0 µmol, 1.0 mol%). The tube was sealed with a rubber septum and immersed in a dry ice/acetone bath at  $-78^{\circ}$ C. A balloon filled with ethylene gas was connected to a long needle, which was inserted to the tube through the rubber septum. Roughly 100 ml of ethylene gas was bubbled through the solution over a time period of approximately 5 minutes, and excess gas was released through the side arm, all while avoiding exposure to light. The valve of the side arm was closed, and the needle was withdrawn from the solution but remained in the headspace of the vessel. The reaction mixture was then subjected to irradiation by one Kessil PR160-390 nm LED with 100% intensity (40 W, ~6 cm away) for a period of ranging from 2 to 15 minutes, all while maintaining the bath temperature at  $-78^{\circ}$ C. The progress of the reaction was monitored at 2, 5, 10, and 15 min by <sup>1</sup>H NMR spectroscopy. The complete conversion of arylthianthrenium salt was confirmed by comparing the <sup>1</sup>H NMR spectrum of the crude reaction mixture with that of pure arylthianthrenium salt, with particular attention to the disappearance of the characteristic doublet peak at around 8.6 ppm, typically occurring within 5 minutes. Then, nucleophile (0.24 mmol, 1.2 equiv) and base (0.40 mmol, 2.0 equiv) were added. The resulting mixture was stirred for 12 h without exposure to light. During this period, the reaction temperature was gradually allowed to rise to 23 °C. In certain cases, heating and solvent changes were required as part of the process. Subsequently, silica gel (5–10 mL) was added, and the reaction mixture was concentrated to dryness under reduced pressure. The resulting residue was purified by chromatography on silica gel to afford the desired product.

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### Data availability

All the data generated or analyzed during this study are included in this article and its Supplementary Information.

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### **Author contributions**

Y.C. developed the chemistry, optimized the reaction conditions, and conducted the mechanistic study. Y.C. and T. K. R. explored the substrate scope. T. Z. and C. K. designed, performed and analysed transient absorption data and related spectroscopic mechanism studies. B. L. and Y. C. performed the DFT calculations. Y.C., T. Z., C. K., and T.R. wrote the manuscript, with contributions from all authors. T.R. directed the project.

### **Competing interests**

TR may benefit from thianthrenium-related sales.

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