Article

Energy-transfer-enabled photocatalytic transformations of aryl thianthrenium salts

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Aryl thianthrenium salts are valuable in photocatalysis but traditionally require external electron donors for activation. This study introduces an energy transfer (EnT) strategy for the activation of aryl thianthrenium salts using 2,3,4,5,6-penta(carbazol-9-yl)benzonitrile (5CzBN) as a metal-free photo-catalyst, eliminating the need for external donors. Utilizing this EnT approach, we achieve C–H deuteration of arenes under visible light with $CDCl_3$ as a deuterium source to synthesize various deuterated aromatic compounds, including important natural products and pharmaceuticals. Additionally, this strategy enables diverse functionalizations including borylation, arylation, cyanation, and selenylation, enhancing the applicability of aryl sulfonium salts in environmentally friendly photocatalysis.

Since the introduction of the Meerwein reaction[1], aryl radicals have emerged as versatile intermediates in organic synthesis, instrumental in the assembly of complex natural products, pharmaceuticals, and advanced functional materials[2,3]. Traditionally, the generation of aryl radicals relied on stoichiometric quantities of reagents, such as AIBN/n-Bu$_3$SnH for aryl halides[4], or the use of stoichiometric transition-metal reductants for diazonium salts[5–7]. Recently, the emergence of visible-light-mediated photocatalysis has revolutionized synthetic chemistry by offering innovative and environmentally friendly approaches to bond formation[8–14]. These photocatalytic methods often generate reactive open-shell species that serve as pivotal intermediates for the formation of assorted chemical bonds[15–19]. Especially, aryl thianthrenium salts have garnered significant interest in recent years as versatile reagents due to their stability, ease of handling, and the ability to be synthesized directly without the need for laborious silica column purification[20–24]. With their positively charged sulfur centers, aryl thianthrenium salts are especially adept at engaging in visible-light-induced organic reactions, acting as one-electron electrophiles[25,26]. Extensive research endeavors have focused on the photocatalytic activation of these salts, either facilitated by a photocatalyst-mediated single electron transfer (SET) mechanism (Fig. 1a) or through the formation of electron donor-acceptor (EDA) complexes (Fig. 1b)[27–30]. These pathways facilitate the formation of C−C and C−X (P, S, O, N) bonds[31–35]. However, it is essential to recognize that the photocatalytic single-electron reduction of aryl thianthrenium salts typically relies on stoichiometric electron donors. This

reliance can lead to increased expenses and intricacies, as well as the possibility of undesired byproducts.
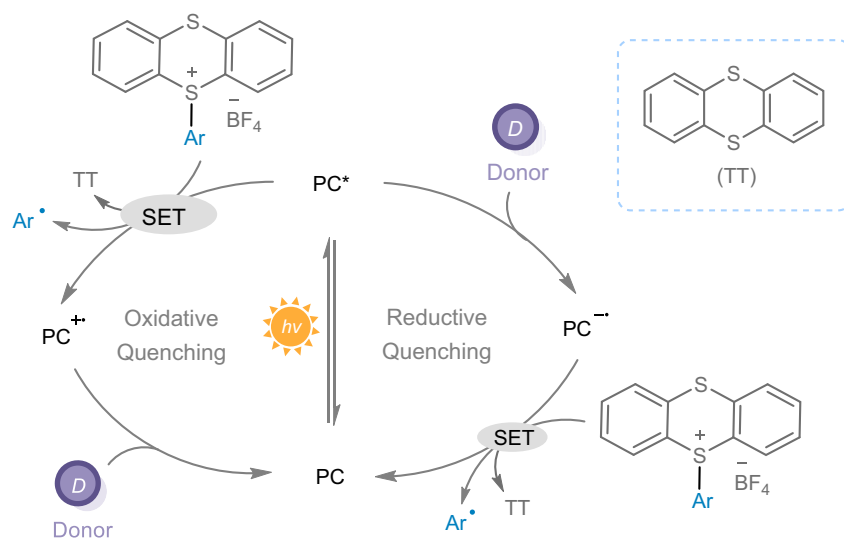
The incorporation of deuterium into organic molecules has attracted significant attention over the past decades[36–42], due to the potential to enhance their stability and pharmacokinetic properties[43–48]. Herein, we disclosed an energy transfer (EnT) strategy for the photoactivation of aryl thianthrenium salts, thereby eliminating the dependency on external electron donors (Fig. 1c). This method facilitates the deuteration process using cost-effective $CDCl_3$ as a deuterium source, resulting in deuterium incorporation into the target compounds including various natural products and pharmaceuticals with good yields. This EnT photoactivation methodology is further applied in other transformations of aryl sulfonium salts, such as borylation, arylation, cyanation, and selenylation. These findings will enhance the photocatalytic transformation of aryl sulfonium salts, indicating a more environmentally benign synthetic strategy for the construction of complex molecular architectures, including essential pharmaceutical compounds.

Results

Reaction optimization

Our study was initiated with the deuteration of thianthrenium salt **1**, as presented in Table 1. Extensive optimization studies demonstrated that employing 5CzBN as a photocatalyst along with $CDCl_3$ as the deuterium source, utilizing H_2O as the solvent, and exposing the reaction mixture to 427 nm light irradiation for 6 hours under atmospheric conditions resulted in the successful isolation of the
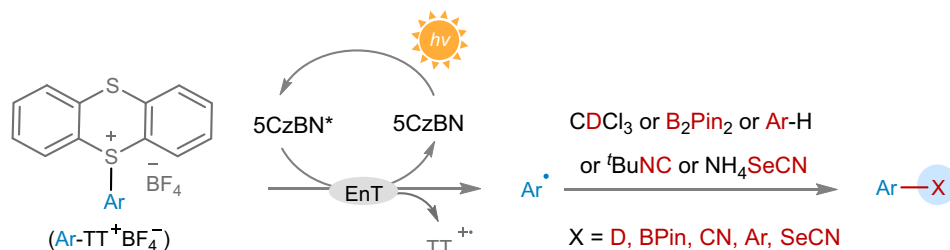
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a) SET Process for Photocatalytic Activation of Aryl Thianthrenium Salts

b) EDA Complexes for Photocatalytic Activation of Aryl Thianthrenium Salts
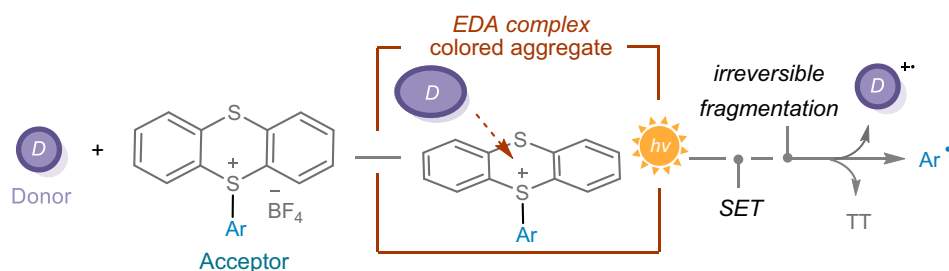
c) Energy Transfer Strategy (This work)
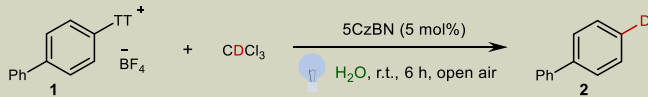

Unexplored Photoactivation Mode of Aryl Thianthrenium Salts

Fig. 1 | Visible-light activation of aryl thianthrenium salts to aryl radicals. a Single electron transfer (SET) process. **b** Electron donor-acceptor (EDA) complexes. **c** This work: energy transfer strategy.

desired product **2** with 82% yield (entry 1). In this reaction, the lower bond dissociation energy (BDE) of CHCl₃ [BDE$_{C-H}$ (CHCl₃) = 93.8 kcal/mol][49] compared to benzene's bond dissociation energy [BDE$_{C-H}$ (benzene) = 113.5 kcal/mol][50] makes deuterium atom abstraction between aryl radical and CDCl₃ thermodynamically favorable[51]. Water serves as an appropriate solvent that does not interfere with the incorporation of deuterium into the product, owing to its relatively high bond dissociation energy [BDE$_{O-H}$ (H₂O) = 118.8 kcal/mol]. Although 5CzBN has not been widely applied as a photocatalyst, the characterization of its photophysical properties indicates that it possesses favorable redox potentials and excited triplet-state energy[52]. Other photocatalysts, including Methylene Blue, Eosin Y, Ir-photocatalysts, 4CzIPN, PTH, and Rhodamine B, showed poor efficiency in this transformation

(entries 2-8). The well-known EnT photocatalysts, such as thioxanthone and benzophenone[53], can effectively catalyze the deuteration reaction under a 390 nm LED irradiation, while under 427 nm light irradiation the desired product was obtained in 11% and 10% yields, respectively (entries 9 and 10). Solvent screening demonstrated that deuterium incorporation was substantially reduced in solvents such as DMSO, THF, and CH₃CN, likely a consequence of their relatively lower BDEs (entries 11-13). Further refinement of the deuterium source confirmed that the deuteration procedure was compatible with CD₂Cl₂, acetonitrile-d₃, and acetone-d₆ to yield the desired product **2** in moderate yields with high deuterium incorporation (entries 14-16). However, DMSO-d₆, D₂O, and methanol-d₄ were not efficient deuterium sources (entries 17-19). Control experiments executed in the absence of 5CzBN or

Table 1 | Variation of standard conditions[a]

Entry	Variation from the conditions	Yield (%)	D-inc (%)
1	None	83	>99
2	Methylene blue instead of 5CzBN	trace	n.d.
3	Eosin Y instead of 5CzBN	trace	n.d.
4	Ir(dFppy)$_3$ instead of 5CzBN	21	>99
5	Ir(p-CF$_3$-ppy)$_3$ instead of 5CzBN	18	>99
6	4CzIPN instead of 5CzBN	<5	n.d.
7	PTH instead of 5CzBN	trace	n.d.
8	Rhodamine B instead of 5CzBN	trace	n.d.
9	Thioxanthone instead of 5CzBN	11 (76)[b]	>99
10	Benzophenone instead of 5CzBN	10 (68)[b]	>99
11	DMSO instead of H$_2$O	55	17
12	THF instead of H$_2$O	64	15
13	CH$_3$CN instead of H$_2$O	23	34
14	CD$_2$Cl$_2$ instead of CDCl$_3$	57	>99
15	Acetone-d$_6$ instead of CDCl$_3$	55	>99
16	Acetonitrile-d$_3$ instead of CDCl$_3$	38	>99
17	DMSO-d$_6$ instead of CDCl$_3$	trace	n.d.
18	D$_2$O instead of CDCl$_3$	trace	n.d.
19	Methanol-d$_4$ instead of CDCl$_3$	n.d.	n.d.
20	Without visible-light irradiation	n.d.	—
21	Without 5CzBN	n.d.	—

[a]Reaction conditions: **1** (0.2 mmol), 5CzBN (5 mol%), CDCl$_3$ (1 mL), H$_2$O (1 mL) were irradiated with 40 W blue LED (427 nm) under open-air atmosphere, GC yields were given based on **1** using mesitylene as an internal standard. Deuterium incorporation (D-inc) was calculated by ^{1}H NMR. n.d. = not detected. 5CzBN = 2,3,4,5,6-penta(carbazol-9-yl)benzonitrile. [b]The reaction was irradiated under 390 nm LED (40 W).

light resulted in the non-detection of the desired product **2** (entries 20 and 21), thereby underscoring the indispensable roles of the photocatalyst and light irradiation.
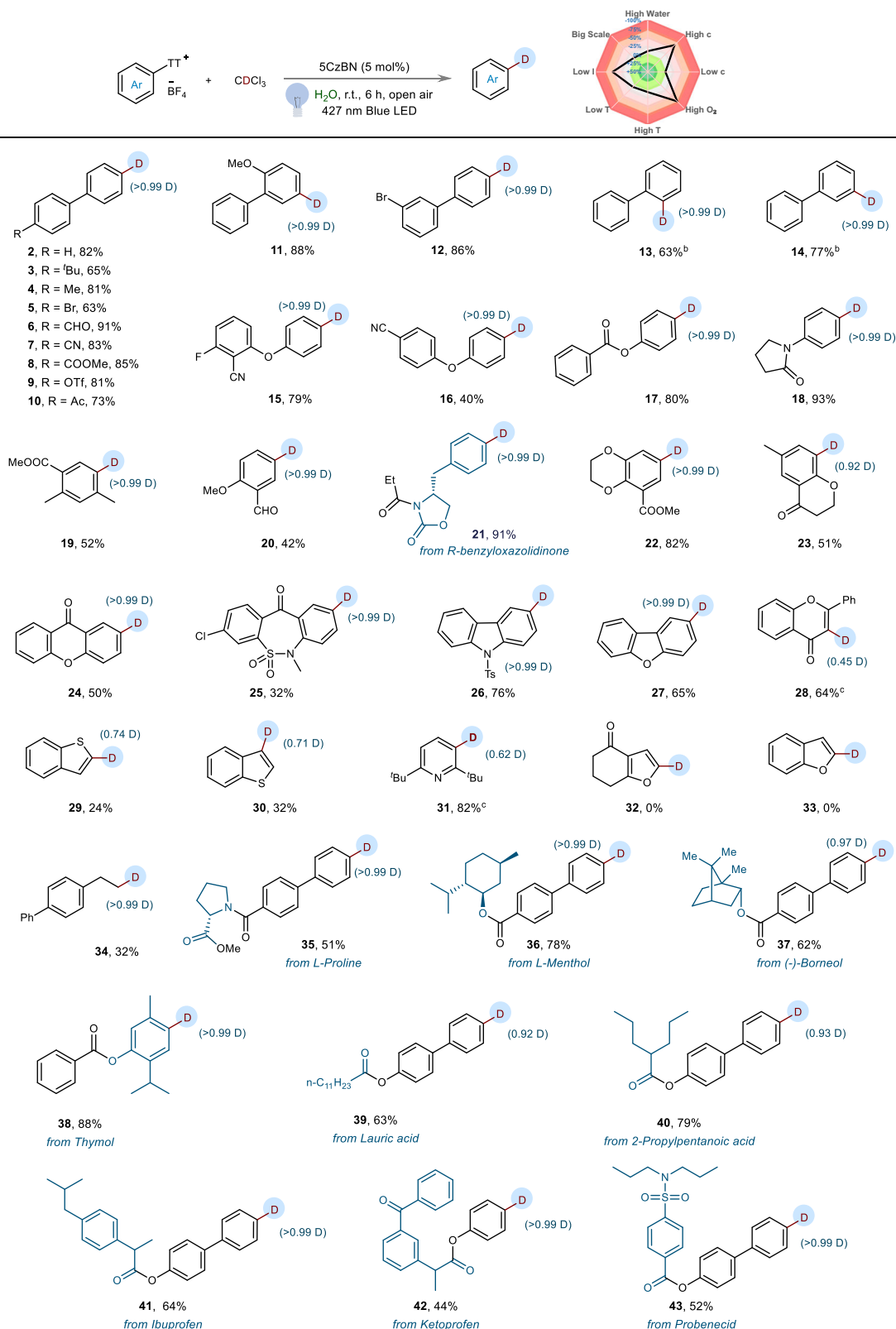
Substrate scope

After optimizing the reaction conditions, a comprehensive investigation was conducted to assess the compatibility of the photocatalytic deuteration reaction (Fig. 2). Notably, a wide range of thianthrenium salts, derived from simple biphenyls, are suitable substrates under the mild reaction conditions. The deuterated products **2-12** bearing various functional groups, including tertiary butyl (-^{t}Bu, **3**), methyl (-Me, **4**), bromo (-Br, **5** and **12**), aldehyde (-CHO, **6**), cyano (-CN, **7**), methyl ester (-COOMe, **8**), triflate (-OTf, **9**), acetyl (-COMe, **10**) and methoxy (-OMe, **11**) were isolated with good yields (63-91%) and excellent deuterium incorporation (>99%). Additionally, this protocol enabled the incorporation of a deuterium atom at either the 2- or 3-positions of the biphenyl, leading to the formation of products **13** and **14** with yields of 63% and 77%, respectively. Furthermore, aromatic ethers or ester compounds also gave the products **15-17** with moderate to good yields. Moreover, benzene compounds with various sensitive functional groups demonstrated suitability for this reaction, resulting in the formation of desired products **18-21** with 42-93% yields.

Due to the importance of heterocyclic structural motifs[54], we further examined the reactivities of heteroatom-containing aryl thianthrenium salts. The corresponding deuterated products **22-31** were isolated in 24–82% yields. However, the substrates containing furan (**32**) and benzofuran (**33**) are not suitable for this procedure. Besides that, alkyl thianthrenium salt was converted into the desired product **34** in 32% yield. Furthermore, aromatic monopeptide displayed notable reactivity under standard conditions,

ultimately leading to the desired product **35** with satisfactory yield. Moreover, derivatives of certain natural products, such as L-Menthol, (-)-Borneol, Thymol, and Lauric acid, were also good substrates in this visible-light-promoted deuteration reaction, affording products **36-43** with 51–88% yields. In these cases, the moderate yields of **16** and **34** might be caused by the formation of by-products, produced through the halogen-atom transfer (XAT) process between aryl/alkyl radicals and CDCl$_3$ (refer to Supplementary Methods for details). The scale-up experiments were further conducted and the results showed that products **2** and **9** could be isolated in 71% yield (0.66 g) and 61% yield (1.1 g), respectively. These promising results indicate the robustness and scalability of our method, highlighting its potential for practical applications on a larger scale (Supplementary Figs. 6 and 7). The sensitivity evaluation radar diagram revealed that the transformation being studied is highly influenced by three key factors: reaction concentration, oxygen levels, and light intensity. These factors were found to have a substantial impact on the reproducibility of the experiment (Supplementary Table 1).

By selectively introducing deuterium atoms at specific positions within a drug molecule, researchers can methodically analyze and quantify metabolic processes, identify potential metabolites, and evaluate the compound's overall stability and pharmacological properties[55–57]. Motivated by the remarkable compatibility of this protocol, we subsequently investigated its applicability for the late-stage modification of natural products, medicinal compounds, and other bioactive molecules (Fig. 3). The derivatives of various complex pharmaceuticals, including Fenofibrate (a hypolipidemic agent), (R)-Tomoxetine (an attention deficit hyperactivity disorder medication), Etofenprox (an insecticide), and Boscalid (an active
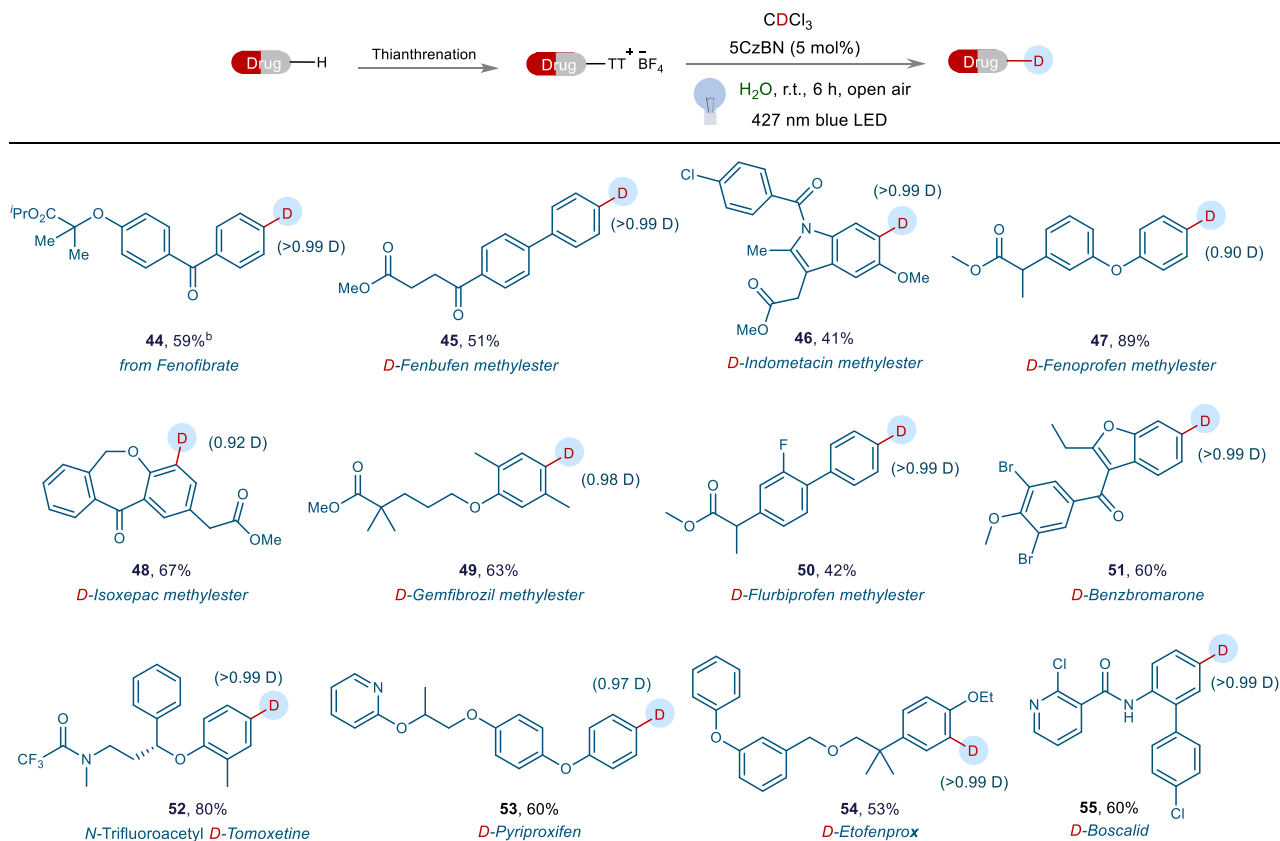
Fig. 2 | Substrate scope and the sensitivity assessment. [a]Reaction conditions: aryl thianthrenium salts (0.2 mmol), 5CzBN (5 mol%), water (1 mL), and CDCl₃ (1 mL) were irradiated with 427 nm blue LED for 6 h. [b]Irradiated for 24 h. [c]5-(aryl)dibenzothiophenium triflate was used.

ingredient), were found to be compatible with this transformation. The desired products **44**-**55** were obtained in good yields with a high deuterium incorporation rate.

Motivated by the promising results, we subsequently applied this energy transfer methodology to the transformations of aryl thianthrenium salts. As depicted in Fig. 4a, the borylation process was observed with the use of bis(pinacolato)diboron (B₂Pin₂) as the boron source, affording the product **56** in 91% yield. Moreover, the cyanation of the aryl thianthrenium salt with *tert*-butyl isocyanide was successfully achieved to deliver 4-phenylbenzonitrile **57** in 52% yield. The

Fig. 3 | Deuteration of bioactive molecules. [a]Reaction conditions: aryl thianthrenium salts (0.2 mmol), 5CzBN (5 mol%), water (1 mL), and CDCl$_3$ (1 mL) were irradiated under 427 nm blue LED for 6 h. [b]Irradiated for 24 h.

reaction between thianthrenium salt **1** and azauracil effectively produced **58** in 72% yield. Additionally, selenocyanation can also be achieved to provide the desired product **59** in 83% yield. Our study underscores the robustness of energy transfer as a strategic approach in chemical synthesis, particularly for activating aryl thianthrenium salts and facilitating diverse bond formations. Besides that, we also applied this method to the synthesis of dideuterated biphenyl **60**, further showcasing the synthetic potential of this approach (Fig. 4b).
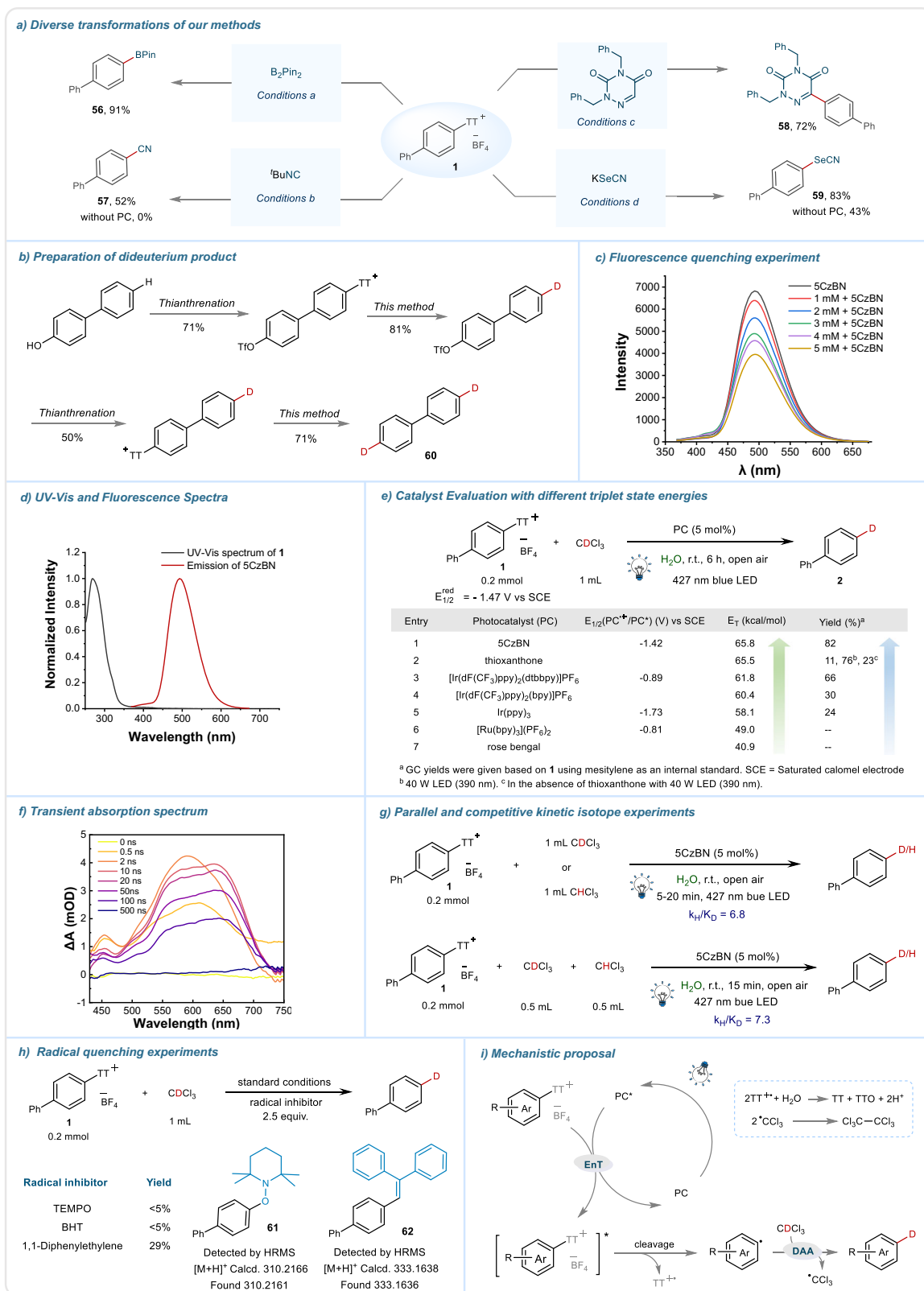
Mechanism

To gain a comprehensive understanding of the reaction mechanisms, extensive experimental investigations were conducted. Initially, fluorescence quenching experiments were performed to confirm the interaction between the photocatalyst 5CzBN and thianthrenium salt **1**. The Stern-Volmer plot shown in Fig. 4c and Supplementary Fig. 10 revealed a significant quenching of the photocatalyst fluorescence by thianthrenium salt **1**, with a discernible linear relationship observed between the fluorescence intensity ratios (I$_0$/I) and the concentrations of thianthrenium salt **1**. The Stern-Volmer constant (K$_{SV}$) was determined to be 0.134 mM^{-1}. Subsequently, absorption spectra of the thianthrenium salt **1** were recorded in CDCl$_3$ (Fig. 4d). The maximum absorption wavelength (λ_{max}) was identified as 290 nm, which is significantly lower than the wavelength of the visible light employed (427 nm). Importantly, the chloroform solution of biphenyl thioxanthene salt exhibited negligible absorption at 427 nm, suggesting that the biphenyl thioxanthene salt cannot be directly excited by the utilized light source. When the absorption band was superimposed on the emission spectra of the 5CzBN catalyst, a negligible overlap was observed, rendering the occurrence of Förster resonance energy transfer improbable[58,59].

DFT calculations revealed that the triplet energy of thianthrenium salt **1** is approximately 60.9 kcal/mol (refer to Supplementary Methods for details), which closely matched that of the

photocatalyst 5CzBN. When typical photocatalysts were applied in the reaction, a clear correlation pattern was observed that photocatalysts with higher triplet energies were linked to increased product yields. Notably, photocatalysts with triplet energy (E$_T$) ≥ 61.8 kcal/mol exhibited product yields exceeding 60% (Fig. 4e, entries 1–3). Moreover, the photocatalyst (Ir[dF(CF$_3$)ppy)$_2$(dtbbpy)] PF$_6$, despite theoretically lacking the reducing capacity required to convert thianthrenium salt into an aryl radical, remarkably enabled the synthesis of product **2** in 66% yield (Fig. 4e, entry 3). In contrast, *fac*-Ir(ppy)$_3$, expected to efficiently reduce thianthrenium salt **1**, only achieved product **2** with 24% yield (Fig. 4e, entry 5). These findings suggest that in the photoactivation of aryl thianthrenium salts the triplet energy state of photocatalyst plays a pivotal role rather than its reductive potential. The low yield (11%) of the thioxanthone-photocatalyzed reaction is attributed to the limited absorption of thioxanthone at 427 nm light. In contrast, when the reaction was irradiated by 390 nm light, an enhanced yield (76%) was observed. In the absence of thioxanthone, the yield diminished to 23%, probably due to product degradation under high-energy UV radiation. Transient absorption studies reveal that the photoreaction of the triplet 5CzBN with thianthrenium salt **1** results in a subtle absorption signal in the 420–460 nm range (Fig. 4f). This observation might be attributed to the formation of the triplet state of thianthrenium salt **1**. More importantly, a prominent absorption signal in the 500–700 nm indicates the presence of TT$^{•+}$[60]. The detection of TT$^{•+}$ provides compelling direct evidence for the energy transfer process between triplet 5CzBN and thianthrenium salt **1**.

Additionally, a light on/off experiment was conducted to assess the light's impact on the reaction. As illustrated in Supplementary Fig. 15, the cessation of the reaction in dark conditions underscored the indispensable role of light, indicating that a radical chain pathway may be excluded. Kinetic isotope effect (KIE) experiments

a) Diverse transformations of our methods

B_2Pin_2
Conditions a

56, 91%

^tBuNC
Conditions b

57, 52%
without PC, 0%

1

Conditions c

58, 72%

KSeCN
Conditions d

59, 83%
without PC, 43%

b) Preparation of dideuterium product

Thianthrenation
71%

This method
81%

Thianthrenation
50%

This method
71%

60

c) Fluorescence quenching experiment

- 5CzBN
- 1 mM + 5CzBN
- 2 mM + 5CzBN
- 3 mM + 5CzBN
- 4 mM + 5CzBN
- 5 mM + 5CzBN

Intensity / λ (nm)

d) UV-Vis and Fluorescence Spectra

- UV-Vis spectrum of **1**
- Emission of 5CzBN

Normalized Intensity / Wavelength (nm)

e) Catalyst Evaluation with different triplet state energies

1
0.2 mmol
$E_{1/2}^{red}$ = - 1.47 V vs SCE

CDCl$_3$
1 mL

PC (5 mol%)
H_2O, r.t., 6 h, open air
427 nm blue LED

2

Entry	Photocatalyst (PC)	$E_{1/2}(PC^{\cdot+}/PC^*)$ (V) vs SCE	E_T (kcal/mol)	Yield (%)[a]
1	5CzBN	-1.42	65.8	82
2	thioxanthone		65.5	11, 76[b], 23[c]
3	[Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$	-0.89	61.8	66
4	[Ir(dF(CF$_3$)ppy)$_2$(bpy)]PF$_6$		60.4	30
5	Ir(ppy)$_3$	-1.73	58.1	24
6	[Ru(bpy)$_3$](PF$_6$)$_2$	-0.81	49.0	--
7	rose bengal		40.9	--

[a] GC yields were given based on **1** using mesitylene as an internal standard. SCE = Saturated calomel electrode
[b] 40 W LED (390 nm). [c] In the absence of thioxanthone with 40 W LED (390 nm).

f) Transient absorption spectrum

- 0 ns
- 0.5 ns
- 2 ns
- 10 ns
- 20 ns
- 50ns
- 100 ns
- 500 ns

ΔA (mOD) / Wavelength (nm)

g) Parallel and competitive kinetic isotope experiments

1
0.2 mmol

1 mL CDCl$_3$
or
1 mL CHCl$_3$

5CzBN (5 mol%)
H_2O, r.t., open air
5-20 min, 427 nm bue LED

k_H/K_D = 6.8

1
0.2 mmol

CDCl$_3$
0.5 mL

CHCl$_3$
0.5 mL

5CzBN (5 mol%)
H_2O, r.t., 15 min, open air
427 nm bue LED

k_H/K_D = 7.3

h) Radical quenching experiments

1
0.2 mmol

CDCl$_3$
1 mL

standard conditions
radical inhibitor
2.5 equiv.

Radical inhibitor	Yield
TEMPO	<5%
BHT	<5%
1,1-Diphenylethylene	29%

61
Detected by HRMS
[M+H]$^+$ Calcd. 310.2166
Found 310.2161

62
Detected by HRMS
[M+H]$^+$ Calcd. 333.1638
Found 333.1636

i) Mechanistic proposal

PC*
$2TT^{\cdot+} + H_2O \longrightarrow TT + TTO + 2H^+$
$2^{\cdot}CCl_3 \longrightarrow Cl_3C{-}CCl_3$

EnT

PC

cleavage
DAA

Fig. 4 | Synthetic applications and mechanistic investigations. a Diverse transformations of our methods. See Supplementary Methods for specific reaction details. **b** The synthesis of dideuterated biphenyl. **c** Fluorescence quenching experiment. **d** UV-Vis and fluorescence spectra. **e** Catalyst evaluation with different triplet stale energies. **f** Transient absorption spectrum of thianthrenium salt **1** in the presence of 5CzBN. **g** Parallel and competitive kinetic isotope experiments. **h** Radical quenching experiments. **i** Mechanistic proposal, DAA = deuterium atom abstraction.

were performed to determine the rate-limiting step in the reaction. The obtained KIE values of 6.8 for parallel reactions and 7.3 for competitive reactions suggest that the rate-limiting step is associated with the cleavage of the C-H bond in CDCl$_3$ (Fig. 4g). Finally, a series of radical quenching experiments were carried out by adding different radical inhibitors, namely 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO), 2,6-*di*-tert-butyl-4-methylphenol (BHT), or 1,1-diphenylethylene, into the reaction system under controlled conditions (Fig. 4h). The addition of these scavengers considerably hindered the progression of the reaction. Moreover, the identification of adducts **61** and **62** through high-resolution mass spectrometry (HRMS) suggests that aryl radicals may be involved in this process.

Based on the aforementioned findings, we proposed the mechanism as depicted in Fig. 4i. The process initiates with the photoactivation of the photocatalyst (PC) upon illumination, generating an excited triplet state (PC*). PC* is subsequently quenched by aryl thianthrenium salts via triplet-triplet energy transfer. Consequently, the excited triplet state of aryl thianthrenium salts is generated while the photocatalyst returns to its ground state. In this excited state, controlled C–S bond cleavage occurs to form aryl radicals and thianthrene radical cations. The aryl radicals then undergo deuterium atom abstraction (DAA) from CDCl$_3$, resulting in the deuterated products and trichloromethyl radical (•CCl$_3$). The combination of •CCl$_3$ leads to the production of hexachloroethane. In this process, water facilitates the reaction by promoting the conversion of thianthrene radical cations into thianthrene and thianthrene S-oxide[61], which were detected in the reaction mixture.

In conclusion, we have developed a visible-light-induced 5CzBN-catalyzed energy transfer (EnT) strategy for the photoactivation of aryl thianthrenium salts. With this metal-free photocatalytic procedure, the deuteration of aryl thianthrenium salts using CDCl$_3$ as a deuterium source was achieved without the need for external donors. This method has displayed excellent compatibility in the incorporation of deuterium into diverse substrates, including important natural products and pharmaceuticals. Furthermore, this EnT strategy could also be applied in other transformations of aryl thianthrenium salts, such as borylation, arylation, cyanoation, and selenocyanation. Considering the extensive applications and practical advantages of our approach, we anticipate that the methodologies developed in this study will facilitate further innovative advancements in the field of photocatalysis.

Methods

General experimental procedures for the deuteration of aryl sulfonium salts

The synthesis was carried out by combining aryl sulfonium salt **1** (0.2 mmol) with 5CzBN (5 mol%), deuterated chloroform (CDCl$_3$, 1.0 mL), and water (1.0 mL) in a 25 mL reaction vessel. This mixture was irradiated under a 40 W blue LED light source (λ = 427 nm) at room temperature, under open-air conditions for 6 h. After irradiation, the reaction solution was extracted with dichloromethane (3 × 3 mL). The collected organic layers were combined, dried over anhydrous sodium sulfate (Na$_2$SO$_4$), and subsequently concentrated under reduced pressure. The resulting residue was purified via column chromatography on silica gel, employing a gradient of petroleum ether and ethyl acetate as eluents, to yield the target deuteration product.

Data availability

The authors declare that the data relating to the experimental procedures, mechanistic studies, characterization of the products, HRMS data, NMR spectra, and computational studies are available within the article and its Supplementary Information as well as supplementary data. All data are available from the corresponding author upon request. Source data are provided with this paper.

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Author contributions

K.S. and Bing Yu designed and guided this project. C.G. is responsible for the implementation of the experimental work. K.S., X.C., and Bin Yu co-wrote the manuscript. Bing Yu and L.Q. discussed the results and commented on the manuscript. All authors discussed the results and comments on the manuscript.

Competing interests

The authors declare no competing interests.

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