Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2025, **16**, 16559

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 7th July 2025
Accepted 11th August 2025

DOI: 10.1039/d5sc05002b

rsc.li/chemical-science

Thiol-free arene C–H thioesterification enabled by a photoactive electron donor–acceptor complex

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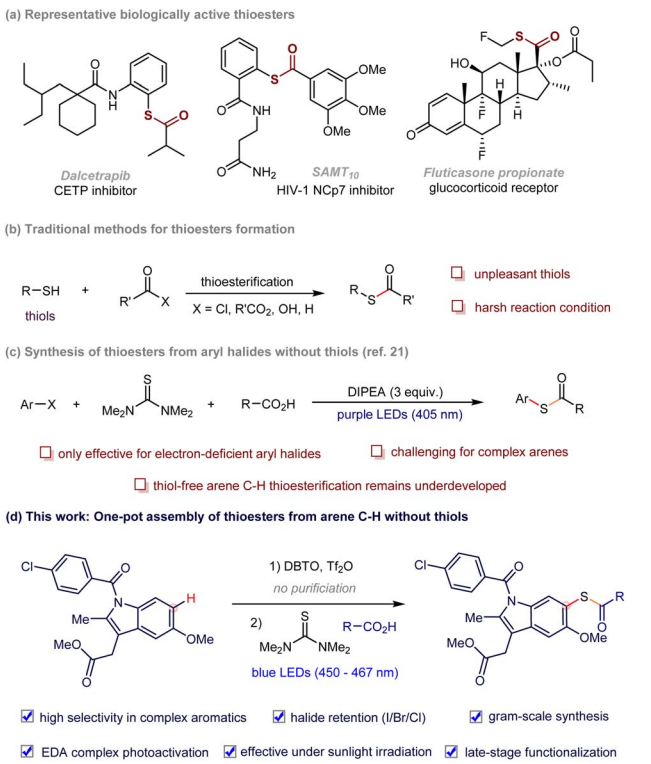
We herein report a catalyst- and thiol-free method for synthesizing thioesters from arenes, carboxylic acids, and tetramethylthiourea in a one-pot process, by combining arene activation *via* the interrupted Pummerer reaction with an electron donor–acceptor complex strategy. The method enables late-stage modification of complex bioactive molecules, and operates effectively under natural sunlight, highlighting its potential synthetic value.

Accessing valuable and high-demand compounds from readily available starting materials under mild, operationally simple conditions is a fundamental goal in synthetic chemistry. Thioesters are not only important scaffolds by themselves, but also serve as key synthetic precursors in organic chemistry, materials science, and pharmaceutical chemistry (Scheme 1a),[1–5] thus making them highly valuable and attracting significant interest. Classical approaches for synthesizing thioester moieties typically involve the acylation of thiols with pre-activated acylating reagents,[6–9] such as carboxylic anhydrides, acyl chlorides, and aldehydes, or the reaction of thiols with carboxylic acids in the presence of harsh dehydrating reagents (Scheme 1b). Additionally, transition-metal catalysis enables efficient thioester synthesis through carbonylative coupling,[10–13] though these methods often require high catalyst loadings, specific ligands, and elevated temperatures to prevent catalyst deactivation by thiols. Despite this considerable progress, they inevitably use thiols as the starting material—characterized by undesirable traits such as unpleasant odor, limited commercial availability, and air instability—which severely limits their practical applications.[14,15] In recent years, there has been growing interest in developing more environmentally benign methods for thioester synthesis that do not rely on thiols or metal catalysts, instead using widely accessible, inexpensive, and stable feedstocks.[16] To this end, various thiol surrogates, such as elemental sulfur (S_8)[17–19] and disulfides,[20] have been explored for thioester synthesis. Notably, Melchiorre's group recently reported an elegant, thiol-free approach for thioester synthesis using aryl halides and carboxylic acids,[21] with odorless and commercially inexpensive tetramethylthiourea as the sulfur source.[22–24] This sulfur source can be activated under high-energy irradiation to acquire reducing power, activating aryl halides to generate aryl radicals *via* single-electron transfer (SET) (Scheme 1c). However, due to the high reduction potential of aryl halides,[25,26] this method is only effective for electron-deficient aryl halides, and is limited to simple aromatic structures due to the difficulty of accessing aryl halides with high chemo- and regioselectivity from complex arenes.[27,28] Thus, the development of efficient,



Scheme 1 Synthetic strategies for thioesters.

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site-selective methods for thioester synthesis with a broad range of arenes, particularly for late-stage functionalization of complex drug scaffolds, remains a challenging yet highly desirable goal.

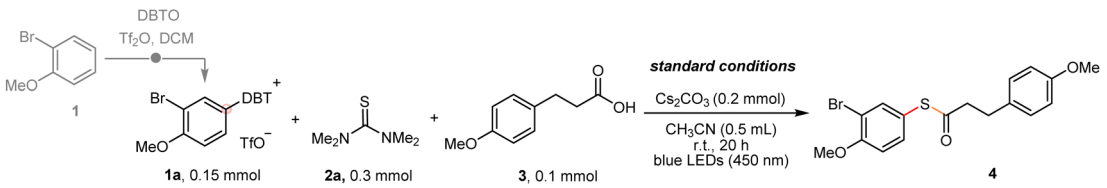
The regioselective interrupted Pummerer activation of arenes with sulfoxides, coupled with the transformation of arylsulfonium salts, has emerged as an efficient and attractive strategy for one-pot arene C–H functionalization.[29–34] This approach formally functionalizes one of the arene C–H bonds with excellent site-selectivity, generating the corresponding arylsulfonium salts.[35–42] It enables the generation of aryl radicals *via* a visible light-induced single-electron transfer or energy transfer process,[43–46] offering higher accessibility compared to their halide counterparts, especially for late-stage functionalization. Notable examples include Procter and colleagues' work on one-pot arene C–H alkylation, cyanation, and arylation,[29–31] and MacMillan's recent report on a versatile and modular method for direct alkylation of native arene C–H bonds, in which aryldibenzothiophenium (DBT) salts were formed *in situ* as aryl radical precursors for radical–radical cross-coupling.[47]

Inspired by these advances and our ongoing interest in electron donor–acceptor (EDA) complex chemistry,[48–52] we herein present a straightforward, catalyst- and thiol-free method for one-pot thioester synthesis from non-prefunctionalized arenes and abundant carboxylic acids. In this system, tetramethylthiourea serves a dual role as both a sulfur source and an electron donor, forming an EDA complex with arylsulfonium salts, thereby facilitating the generation of aryl radicals under visible light irradiation. This protocol successfully installs complex thioester fragments into highly sophisticated aromatic drug scaffolds (Scheme 1d), achieving selectivity, diversity, and practicality that are difficult to match using alternative approaches.

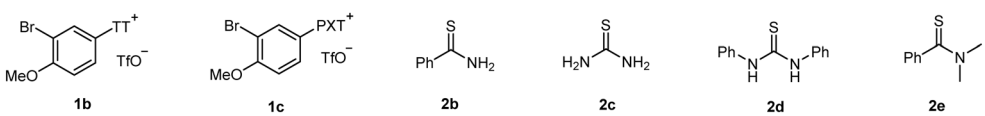
We commenced this study by using arylsulfonium salt **1a** (easily prepared from arene **1**), tetramethylthiourea **2a**, and carboxylic acid **3** as model substrates for thioester synthesis, as outlined in Table 1. After thoroughly investigating all reaction parameters (see the SI for details), we found that a simple mixture of **1a**, **2a**, and **3** with blue light-emitting diodes (blue LEDs, 450 nm) in the presence of Cs_2CO_3 (2.0 equiv.) in acetonitrile (MeCN, 0.2 M) at room temperature for 20 hours, resulted in the target product **4** with a 96% yield (entry 1). Other arylsulfonium salts, such as arylthianthrenium (TT) salt **1b** and arylphenoxathinium (PXT) salt **1c**, were also effective, albeit with lower yields (entry 2). Other sulfur sources (**2b–2e**) proved ineffective in this system (entry 3). Notably, when the wavelength of the irradiated light was increased to 520 nm (green LEDs), the reaction still proceeded with high efficiency (entry 8). This result clearly distinguishes our reaction mechanism from that of Melchiorre's group,[21] which requires purple LEDs (405 nm) to activate tetramethylthiourea for smooth reaction progression, while blue light (465 nm) is ineffective. When using alternative solvents such as 1,4-dioxane, tetrahydrofuran (THF), or *N*-methylpyrrolidin-2-one (NMP) instead of CH_3CN, the reaction efficiency was significantly reduced (entries 4 and 5), likely due to solvent effects that hinder the formation of the transient EDA encounter complex.[53–56] We also tested other organic bases, such as DIPEA (*N*,*N*-diisopropylethylamine) and triethylamine, yielding the target product **4** in 95% and 74% yields, respectively (entry 6). Additionally, reducing the reaction concentration led to a moderate decrease in reaction efficiency (entry 7). Control experiments confirmed that both the base and light were essential for the reaction (entries 9 and 10).

To broaden the applicability of our thioesterification method, we further developed a one-pot sequence for the direct

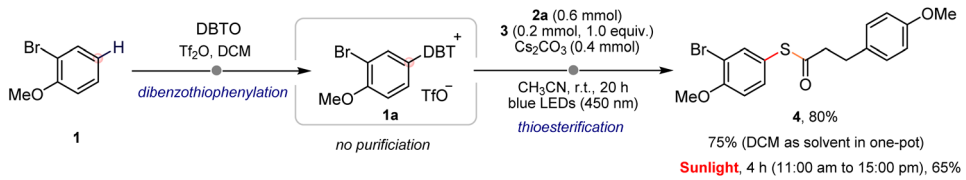
Table 1 Optimization of the reaction conditions[a]



Entry	Variation from standard conditions	Yield of **4** (%)	Entry	Variation from standard conditions	Yield of **4** (%)
1	None	96 (90)	6	DIPEA or NEt_3 instead of Cs_2CO_3	95 or 74
2	**1b**, or **1c** instead of **1a**	66, or 78	7	CH_3CN (1 mL)	80
3	**2b** - **2d**, or **2e** instead of **2a**	n.d., or 12	8	520 nm instead of 450 nm	73
4	THF or dioxane instead of CH_3CN	17 or 26	9	No base	n.d.
5	NMP instead of CH_3CN	trace	10	No light	n.d.



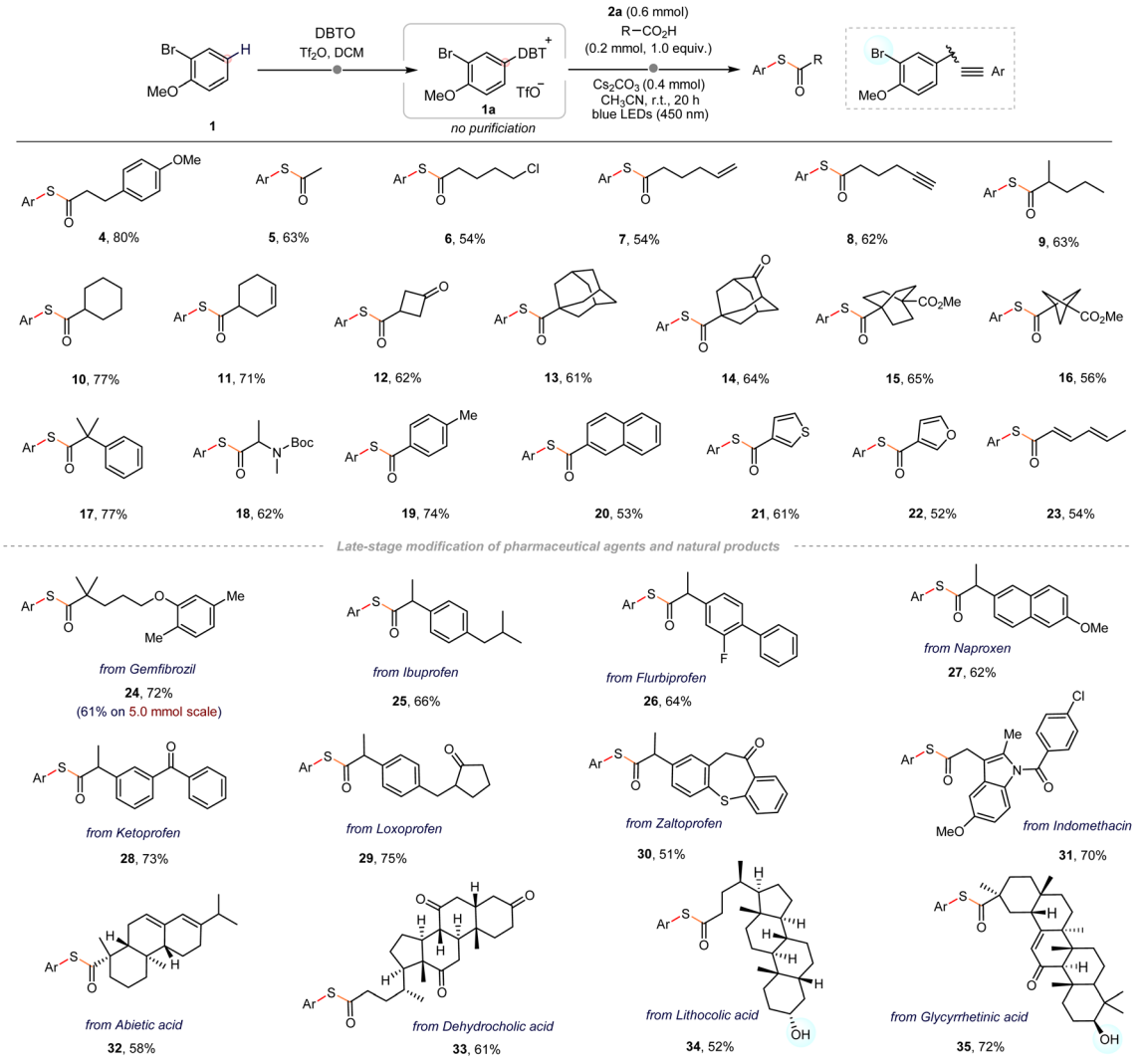
[a] Reaction conditions: **1a** (0.15 mmol, 1.5 eq.), **2a** (0.3 mmol, 3.0 eq.), **3** (0.1 mmol, 1.0 eq.), Cs_2CO_3 (0.2 mmol, 2.0 eq.), CH_3CN (0.5 mL), 20 h, LEDs (450 nm, 18 W), room temperature (r.t.). The yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. n.d.: not detected. DBT = dibenzothiophene.



Scheme 2 One-pot C–H thioesterification sequence directly from unfunctionalized arene **1**.

C–H thioesterification of arene **1**. As shown in Scheme 2, arylsulfonium salt **1a** was generated from arene **1** using dibenzothiophene oxide (DBTO) and triflic anhydride *via* the interrupted Pummerer activation strategy in a telescoped protocol, eliminating the need for additional column purification. Under our optimized thioesterification conditions for the arylsulfonium salt (Table 1, entry 1), the desired product **4** was isolated in an 80% overall yield in one-pot. Notably, when dichloromethane (DCM) alone was used as the solvent throughout the entire reaction, product **4** was still obtained in a 75% yield, further simplifying the operational process. Moreover, the reaction proceeded efficiently under natural sunlight irradiation, yielding the desired product **4** in 65% yield in one-pot.

Table 2 Scope of acids[a]

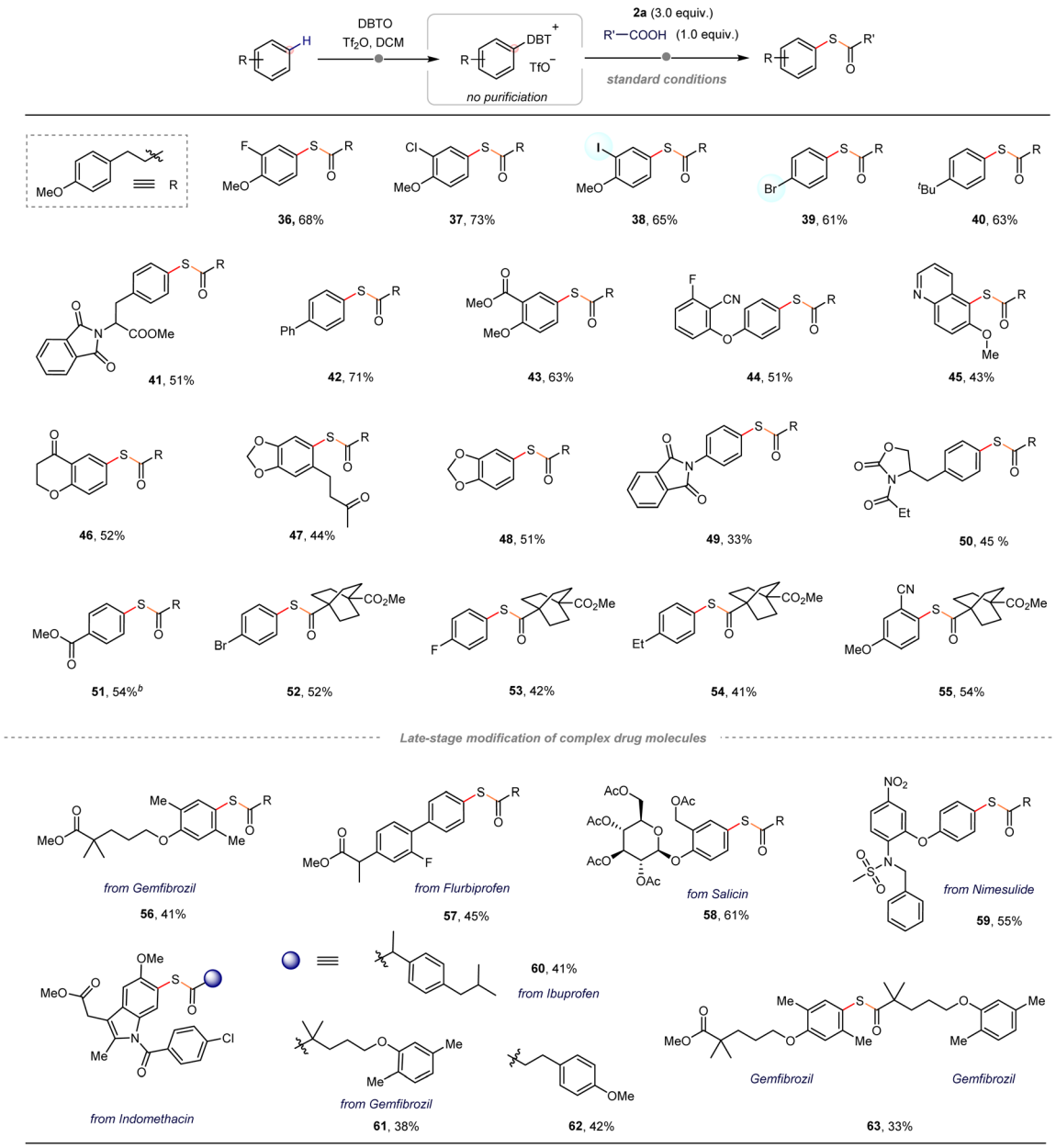


[a] All yields are isolated and reactions were performed on a 0.2 mmol scale with acids (1.0 equiv.); see the SI for full detailed experimental conditions.

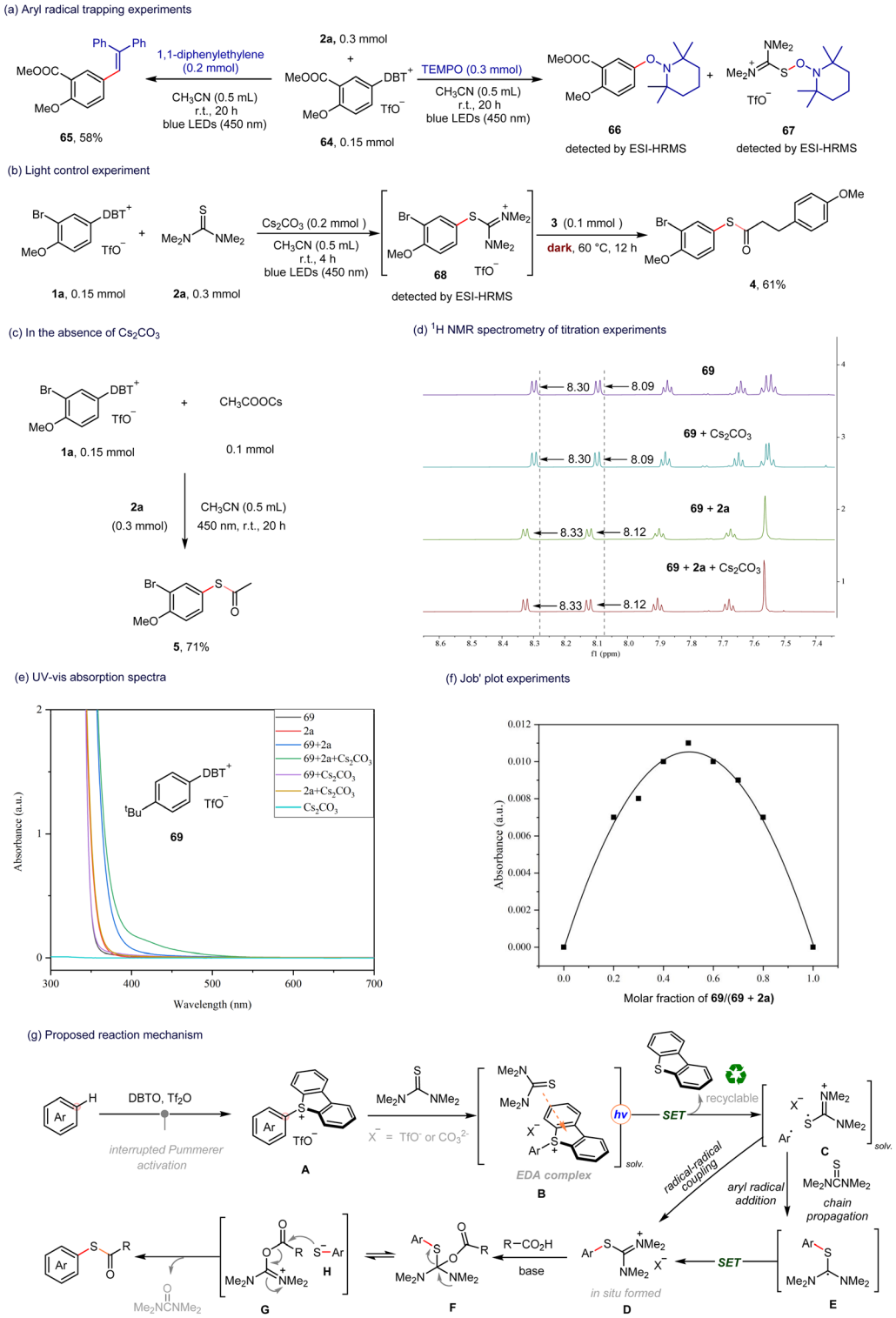
The one-pot procedure outlined in Scheme 2 was employed to evaluate the scope of the thioesterification strategy with diverse carboxylic acids. As shown in Table 2, simple acetic acid was effective to afford the desired thioester **5**. A broad range of primary, secondary and tertiary alkyl carboxylic acids (**4–17**), amino acids (**18**), aromatic acids (**19–22**) and acrylic acid (**23**) were also compatible with this protocol. Functional groups including alkyl chloride (**6**), alkene (**7** and **11**), alkyne (**8**), ketone (**12** and **14**), ester (**15** and **16**), free hydroxyl group (**34** and **35**), and heteroarenes (**21** and **22**), were well tolerated. Notably, structurally complex pharmaceuticals and natural products bearing carboxylic acid groups, such as gemfibrozil (**24**), ibuprofen (**25**), flurbiprofen (**26**), naproxen (**27**), ketoprofen (**28**), loxoprofen (**29**), zaltoprofen (**30**), indomethacin (**31**), abietic acid (**32**), dehydrocholic acid (**33**), lithocolic acid (**34**), and glycyrrhetinic acid (**35**), underwent smooth reactions with excellent functional group compatibility. Furthermore, the one-pot C–H thioesterification sequence scaled efficiently to 5.0 mmol without altering reaction conditions, delivering product **24** in 61% yield, highlighting the significant practical utility.

Next, we investigated the scope of the arene coupling partner to demonstrate the generality of the one-pot, arene C–H

Table 3 Scope of arenes[a]



[a] All yields are isolated and reactions were performed on a 0.2 mmol scale with acids (1.0 equiv.); see the SI for full detailed experimental conditions.
[b] Arylthianthrenium salt was used as a substrate to replace the *in situ* formed aryl-DBT salt.



Scheme 3 Mechanistic studies.

thioesterification protocol (Table 3). Various commercially available arenes with electron-rich/electron-deficient substituents across *ortho*-, *meta*-, and *para*-positions underwent efficient transformations, yielding thioesters (**36–55**) with exceptional site- and chemoselectivity. The protocol tolerated C(sp^2)–halogen (I/Br/Cl) bonds (**37–39**, **52**), highlighting its orthogonality to traditional cross-coupling strategies for further downstream manipulations. Heteroaromatic quinoline was also amenable to this protocol (**45**). Importantly, the mild, redox-neutral conditions provide a valuable tool for precise late-

stage modifications of complex drug molecules. Pharmaceuticals including gemfibrozil (**56**), flurbiprofen (**57**), salicin (**58**), nimesulide (**59**), and indomethacin (**62**) performed well in the C–H thioesterification sequence. Notably, the protocol facilitated the coupling of two structurally distinct building blocks, as exemplified by the coupling of gemfibrozil with gemfibrozil (**63**), and the coupling of indomethacin, an anti-inflammatory drug, with ibuprofen (**60**) or gemfibrozil (**61**), which is unattainable with conventional thioesterification methods.[14,15,21] To our knowledge, this represents the first example of a one-pot, thiol-free arene C–H thioesterification strategy, demonstrating high selectivity, scalability, and substrate diversity.

A series of experimental investigations were conducted to gain insights into the reaction pathway. As shown in Scheme 3a, radical trapping experiments were performed by adding 1,1-diphenylethylene or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as radical scavengers into the reaction system. The radical-trapped products were detected using high-resolution mass spectrometry (HRMS), which indicated the involvement of aryl and thiol radicals in the reaction process, with the generation of these radicals occurring in the absence of a base and acid.[44] Subsequently, control experiments were performed, including irradiation and variation of the order of substrate addition (Scheme 3b). We detected the formation of the isothiouronium ion intermediate **68** by HRMS without adding acid under standard conditions.[21,23,24] When acid **3** was added to the reaction system under dark conditions, we successfully isolated the target product **4**. Furthermore, replacing "acetic acid and Cs_2CO_3" with "cesium acetate (CH_3COOCs)", yielded the desired product **5** in 71% yield (Scheme 3c). These results suggest that the key role of the base is to promote the deprotonation of carboxylic acids to generate carboxylate anions. Additionally, analysis of the ^1H NMR spectra of different reaction components (Scheme 3d) revealed that the addition of tetramethylthiourea **2a** significantly altered the hydrogen shift in the aromatic region of arylsulfonium salt **69**, whereas Cs_2CO_3 had no visible effect. This suggests that the interaction between the arylsulfonium salt and tetramethylthiourea affects the electron cloud distribution on the aromatic ring.[57] The ^1H NMR spectrum of the three-component mixtures (**69**, **2a** and Cs_2CO_3) in the aromatic region closely resembled that of the mixture of **69** and **2a** alone, indicating that the EDA complexes in the reaction system are primarily composed of arylsulfonium salts and tetramethylthiourea. Ultraviolet-visible (UV-vis) studies were also conducted to further confirm the existence of charge-transfer interactions between arylsulfonium salts and tetramethylthiourea. As shown in Scheme 3e, the light absorption wavelengths of individual components (**69**, **2a**, and Cs_2CO_3), and the mixture of **69** with Cs_2CO_3, were all below 400 nm. However, a significant bathochromic shift was observed in the absorption spectrum of the solution containing **69** and **2a**, providing strong evidence for the existence of an EDA complex between the arylsulfonium salt and tetramethylthiourea. The absorption spectra of the reaction mixture (**69**, **2a**, and Cs_2CO_3) exhibited a further red-shift, likely due to the strengthening of intermolecular interactions between **69** and **2a** upon the addition of Cs_2CO_3. The formation of this EDA complex was also confirmed by the Job plot experiments,[44] which established a 1 : 1 stoichiometric relationship between aryl dibenzothiophenium salts and tetramethylthiourea (Scheme 3f). Finally, a quantum yield experiment was conducted to explore the potential reaction pathway for this transformation. The quantum yield was measured as $\Phi = 29.7$, suggesting a radical chain mechanism.

Based on these mechanistic findings and the existing literature,[21,23,30,51] a plausible mechanism for the thiol-free arene C–H thioesterification is proposed in Scheme 3g. Arylsulfonium salt **A** is generated from an arene with DBTO and triflic anhydride by an interrupted Pummerer activation strategy,[30] performed in a telescoped manner without additional column purification. The photoactive EDA complex **B** is then formed between arylsulfonium salt **A** and tetramethylthiourea **2a** in the ground state. Upon visible light irradiation, a SET event triggers a fast and irreversible fragmentation, leading to the generation of dibenzothiophene as a byproduct, which can be recycled as a precursor for arylsulfonium salt synthesis, along with a radical ion pair **C** in a solvent cage. The isothiouronium salt **D** is then formed *in situ* through a radical–radical coupling process. Nucleophilic addition of carboxylate anions to preformed **D** generates a hemithioacetal **F**, which is in equilibrium with the intermediate **G** upon extrusion of thiolate **H**.[21] Transiently formed thiolate **H** then reattacks intermediate **G** *via* a deoxythiolation polar pathway, resulting in the formation of the desired thioesters. Additionally, the aryl radical intermediate interacts with tetramethylthiourea to form the radical intermediate **E**.[24] This intermediate **E** undergoes SET with the arylsulfonium salt, leading to the *in situ* formation of aryl isothiouronium salts **D**, which propagates the chain.

Conclusions

In summary, we have developed a one-pot strategy for synthesizing thioesters from arenes and carboxylic acids by combining substrate activation *via* the interrupted Pummerer reaction with the EDA complex strategy. Mechanistic studies show that tetramethylthiourea acts as both a sulfur source and an electron donor, forming EDA complexes with arylsulfonium salts, which generate aryl radicals upon visible light irradiation. This method offers high chemoselectivity and functional group tolerance, enabling successful late-stage functionalization of complex bioactive molecules and pharmaceuticals. Notably, the protocol is scalable to the gram-scale and operates efficiently under natural sunlight, eliminating the need for specialized photoreactors, thus emphasizing the practicality and scalability of our approach.

Author contributions

Yan-Qiu Jiang: data curation, formal analysis, investigation, methodology, validation, and writing – original draft. Ang Gao: data curation, formal analysis, investigation, and methodology. Ming-Chen Fu: conceptualization, data curation, formal analysis, funding acquisition, investigation, project administration, supervision, writing – original draft, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI. See DOI: **https://doi.org/10.1039/d5sc05002b**.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22101272), the National Youth Talent Program and the Research Start-Up Funds of Hefei University of Technology.

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