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EDA complex photochemistry as a strategy for C–S bond formation

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This review highlights the use of photochemically excited electron donor–acceptor (EDA) complexes as a sustainable, modern approach to carbon–sulfur bond formation. C–S bonds are essential in various fields, including pharmaceuticals, materials science, and agrochemicals, yet traditional synthetic methods often face challenges such as harsh conditions and high costs. EDA complexes, formed through non-covalent interactions between electron-rich donors and electron-deficient acceptors, undergo visible-light-induced single-electron transfer (SET) to generate reactive radical intermediates. These intermediates enable efficient, selective, and environmentally friendly C–S bond formation under mild conditions. The article explores recent examples of practical applications of these reactions, including their mechanism, providing a comprehensive understanding of these cutting-edge methods and their potential to advance sustainable synthetic chemistry.

1. General introduction

Carbon–sulfur bonds hold immense significance in organic chemistry due to their widespread occurrence in biologically active molecules, functional materials, and natural products.[1] Organic compounds featuring C–S bonds (representative classes are shown in Fig. 1) are essential components in pharmaceuticals, agrochemicals, and industrial applications, making their efficient and selective synthesis a cornerstone of modern research.[2] While traditional methodologies for C–S bond formation, such as nucleophilic substitution,[3] metal-catalyzed cross-coupling reactions,[4] and radical-mediated processes,[5] have undergone substantial advancements, many of these approaches are constrained by harsh reaction conditions, reliance on expensive catalysts, or the use of stoichiometric reagents. These limitations often hinder sustainability and restrict compatibility with sensitive functional groups.

In recent years, photochemistry has emerged as a transformative tool in organic synthesis, offering novel pathways to

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Illán Tagarro

Illán Tagarro Peña completed in 2024 a BS in Chemistry at the University of Oviedo. He is currently completing his master studies at the same university under the supervision of Prof. Carlos Valdés and Dr Manuel Plaza. His research is devoted to the development of multicomponent transformations oriented to C–S bond formation that rely on photochemical activation of EDA complexes.

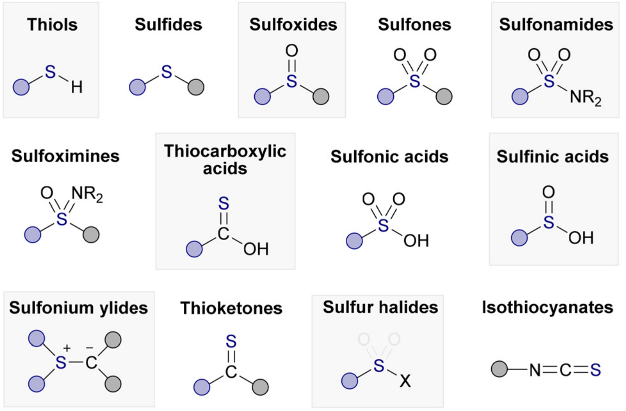
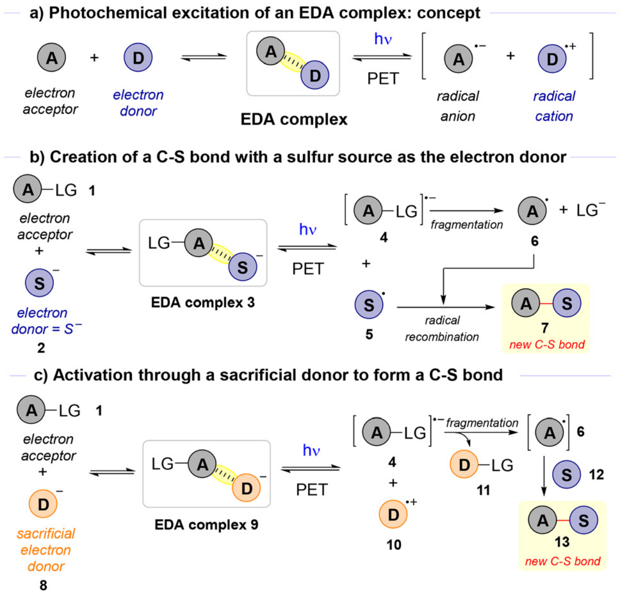


Fig. 1 Representative families of sulfur-containing organic molecules.



Scheme 1 Activation modes through the photochemistry of EDA complexes for C–S bond formation.

access diverse radical-based chemical transformations,[6] including C–S bond formation.[7] A particularly promising innovation in this domain is the utilization of electron donor–acceptor (EDA) complexes to drive photochemical reactions.[8] EDA complexes are non-covalent assemblies formed through supramolecular interactions between an electron-rich donor and an electron-deficient acceptor. Upon absorption of visible light, these complexes are promoted to an electronically excited state, characterized by charge-transfer interactions. This excitation triggers single electron transfer (SET) from the donor to the acceptor, generating a radical ion pair (Scheme 1b). These radical ions are highly reactive intermediates, capable of engaging in a variety of bond-forming processes, including C–C, C–heteroatom, and, notably, C–S bond construction.[9] The SET process is facilitated by the alignment of frontier molecular orbitals (HOMO and LUMO) of the donor and acceptor, ensuring efficient electron transfer. The photochemical strategies based on EDA complexes often circumvent the need for metals, employ readily available and inexpensive starting materials, and operate under mild, ambient conditions. Such features align with the principles of green chemistry, emphasizing sustainability and reduced environmental impact.[10] Moreover, the ability to utilize visible light as a renewable and abundant energy source further highlights the appeal of EDA complex-based photochemical reactions in contemporary synthesis.[11]

Manuel Plaza

Manuel Plaza finished his BS in Chemistry and master's studies at the University of Oviedo in 2014. In 2018, he completed his PhD in Synthesis and Chemical Reactivity at the same university under the supervision of Prof. Carlos Valdés, and subsequently undertook postdoctoral training in photochemistry for three years with Prof. Thorsten Bach at the Technical University of Munich. In 2021, he moved back to the University of Oviedo, where he started his independent career as a Margarita Salas group leader. Currently, he is a Ramón y Cajal assistant professor at the same university. His research focuses on the development of photochemical cross-coupling reactions and photobiocatalytic processes.

Recent studies have illustrated that photochemically activated EDA complexes enable C–S bond formation with remarkable efficiency, selectivity, and functional group compatibility. This review article aims to provide an overview of the burgeoning field of C–S bond-forming reactions enabled by photochemical excitation of EDA complexes, delving into the reaction mechanisms proposed by the authors for such transformations, with a particular focus on the synthesis of small molecules.[12] By advancing the understanding of these innovative strategies, this field has the potential to influence a wide array of disciplines and drive sustainable advancements in synthetic chemistry.

2. Creation of C–S bonds through photochemical excitation of EDA complexes

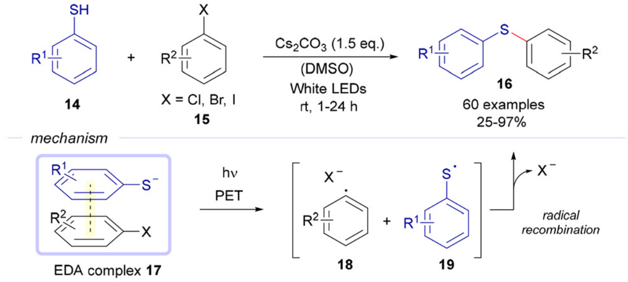
2.1. General mechanisms

As outlined in the introduction, light-driven excitation of an EDA complex typically facilitates a photoinduced electron transfer (PET) from the electron donor to the electron acceptor within the complex. This process results in the formation of a radical ion pair, which can evolve through various pathways to generate new chemical bonds (Scheme 1a).

In the context of photochemical activation of EDA complexes to form C–S bonds, two general mechanisms can be distinguished. In the first, an electron acceptor **1** forms an EDA complex with a nucleophilic sulfur source **2** as the electron donor (Scheme 1b). Upon photochemical excitation, the EDA complex **3** generates a radical anion **4** and a sulfur-centered radical **5**. The radical anion **4**, being unstable, undergoes irreversible fragmentation to produce a new radical species **6** and eliminating a leaving group (LG). Subsequent radical recombination between this newly formed radical **6** and the sulfur-centered radical **5** leads to the formation of a new C–S bond, yielding the final product **7**. Alternatively, the electron acceptor **1** can be activated using a sacrificial electron donor **8**, which does not contain a sulfur motif (Scheme 1c). In this case, the resulting EDA complex **9** generates the radical anion **4** and a radical cation **10** upon excitation. As before, the radical anion **4** fragments to form the radical intermediate **6**, while the salt **11** is produced as a byproduct. It should be noted at this point that catalytic amounts of the sacrificial donor can be used, and this will be contemplated later through specific examples. The radical intermediate **6** is then intercepted by a sulfur-containing radical trapping agent, forming a new C–S bond and yielding the final product **13**. These complementary approaches have been explored extensively by various research groups to synthesize diverse organosulfur compounds, leveraging the unique advantages of EDA complex photochemistry. In the subsequent sections of this review, these reactions will be categorized based on the type of C–S bond formed (Csp^2–S or Csp^3–S). While the mechanistic discussion will be addressed in detail in most of the cases, the analysis of the experimental work that led the authors to propose each mechanism is beyond the scope of this review. Readers seeking a deeper understanding of the specific studies are encouraged to consult the original publications or a review by Prof. Stephenson on mechanistic investigations of EDA complexes.[13]

2.2. C(sp^2)–S bond forming reactions

The most extensively developed and successful chemistry for the photochemical activation of EDA complexes aimed at carbon–sulfur bond formation has undoubtedly focused on C(sp^2)–S bonds.



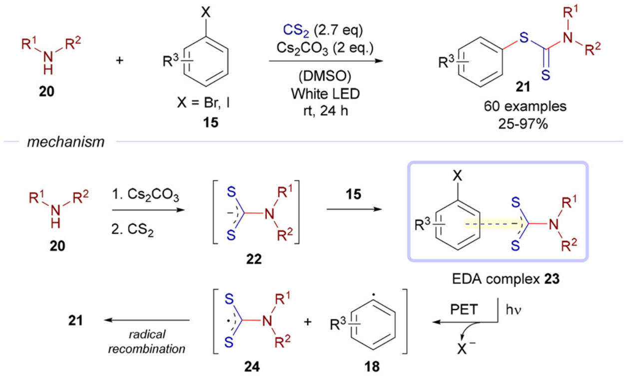
Scheme 2 Photochemical catalyst-free preparation of aryl thioethers **16** from aryl halides **15** and thiophenols **14**.

2.2.1. Nucleophilic sulfur source as the electron donor.

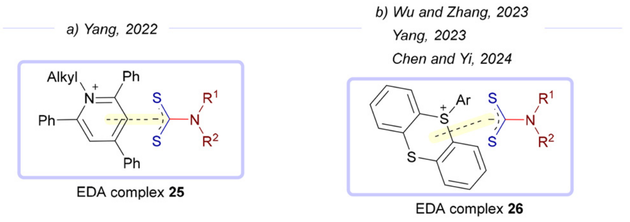
One of the landmark studies on the photochemical activation of EDA complexes for C(sp^2)–S bond formation was reported in 2017 by Miyake and co-workers (Scheme 2).[14] In this study, thiophenols **14** reacted with aryl halides **15** to produce the corresponding thioethers **16**. Mechanistically, the reaction is driven by light-induced activation of the EDA complex **17** formed through π–π stacking interactions between **15** and the deprotonated thiophenol **14**, which generates carbon-centered and sulfur-centered radicals **18** and **19**, respectively, as key intermediates. These radicals undergo subsequent recombination to yield the final thioether products **16**. This work represents a simple photochemical approach under very mild reaction conditions for the preparation of thioethers: only both coupling reagents and base are needed for the cross-coupling, without any catalyst, high temperatures or oxidants being needed.

Following this work, numerous transformations utilizing organic halides as electron acceptors and nucleophilic sulfur species as electron donors were reported. Notably, in 2019, Yang and co-workers developed a synthetic protocol for the preparation of *S*-aryl dithiocarbamates **21** from aryl halides **15**, amines **20**, and carbon disulfide (Scheme 3).[15] Mechanistically, the reaction begins with the generation of an anionic species *via* deprotonation of the amines **20** under basic conditions. This anionic intermediate then reacts with carbon disulfide to form a sulfur-centered anionic species **22**, which acts as the electron donor in the EDA complex **23**, formed with the organic halide **15** as the electron acceptor. Upon photochemical activation, the EDA complex undergoes fragmentation, generating radical intermediates **24** and **18**. These radicals subsequently recombine to yield the desired *S*-aryl dithiocarbamates **21**.

Following the first work by Yang and colleagues, additional EDA-complex-mediated transformations were developed, employing intermediates **22** as electron donors while varying the electron-accepting precursors. In 2022, the same group explored the use of Katriztky salts as electron acceptors (*via* EDA complex **25**; Scheme 4a).[16] More recently, different



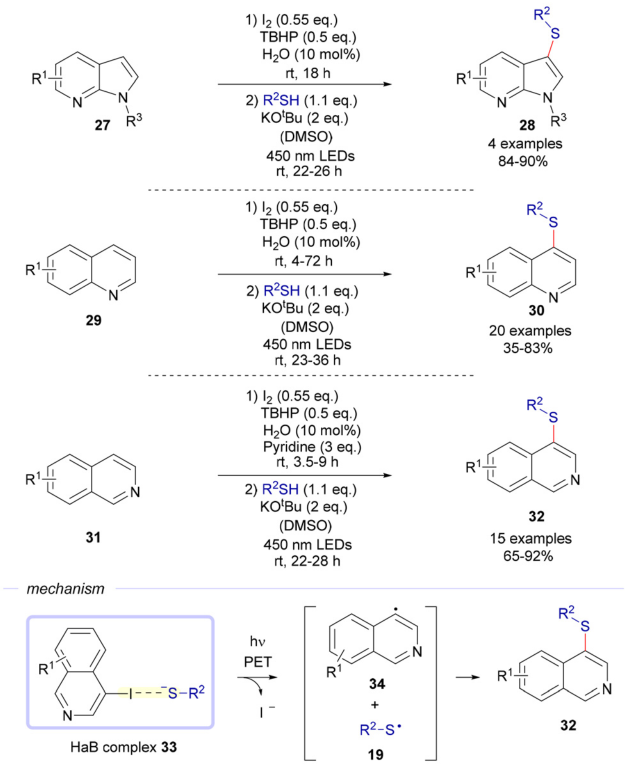
Scheme 3 Light-driven synthesis of aryl *S*-aryl dithiocarbonates **21** from aryl halides **15**, amines **20** and carbon disulfide.



Scheme 4 Dithiocarbamates as electron donors in the reaction between Katriztky salts or thianthrenium salts.

research groups employed thianthrenium salts as alternative reagents in this type of transformation (*via* EDA complex **26**; Scheme 4b).[17] Due to the mechanistic similarities with Yang's earlier work, a detailed discussion of these reactions will be omitted.

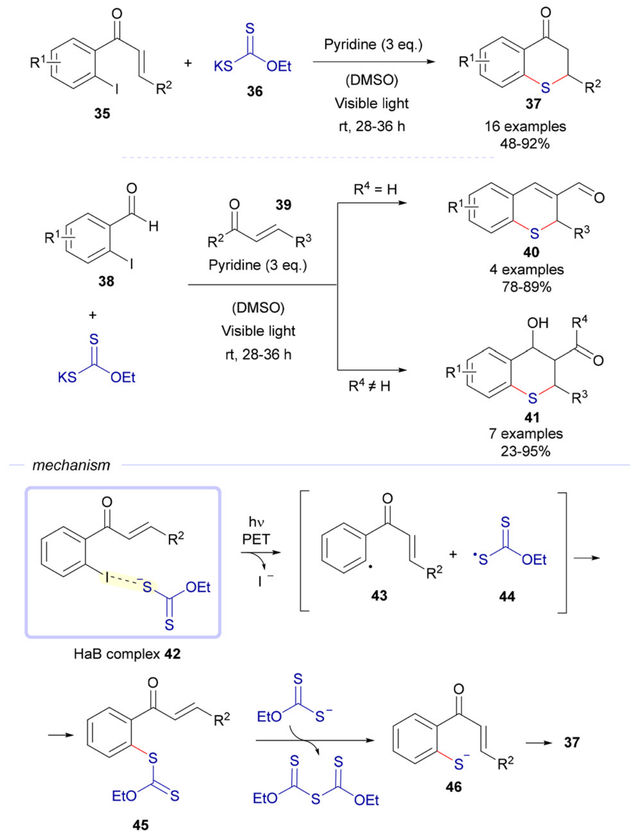
In 2021, Sekar and co-workers introduced a novel method for the direct synthesis of diverse heteroaryl thioethers using a halogen-bonding-initiated photochemical reaction.[18] This reaction is initiated by the photochemical excitation of a halogen-bonding (HaB) complex, which is a specific type of EDA complex. Electron-acceptor molecules that possess a covalently bonded halogen atom typically exhibit a positive electrostatic potential region along the axis of the covalent bond, referred to as a σ-hole.[19] This feature enables the possibility of a non-covalent attractive interaction between an electron-acceptor molecule and an electron donor or nucleophile. This interaction involves a partial n → σ* charge transfer, where electrons from a non-bonding orbital of the electron donor (HaB acceptor, electron donor) are transferred to an antibonding orbital (σ*) of the electron acceptor (HaB donor).[20] The nature of the halogen bond influences significantly the electron transfer efficiency within halogen-bonding-assisted EDA complexes. Due to the greater size of the σ-hole, stronger halogen bonds are formed when more polarizable halogen atoms are involved as the halogen-bond donor (*e.g.*, iodine over bromine or chlorine). Additionally, the electronic environment of the halogen-bond donor (such as electron-withdrawing substituents) modulates the strength of the interaction, thereby impacting the overlap between frontier molecular orbitals with the halogen-bond acceptor, therefore facilitating electron transfer. These factors collectively dictate the efficiency of the halogen-bonding complex formation and subsequent reactivity. In particular, the transformation reported by Sekar, outlined in Scheme 5, proceeds in two distinct steps. Initially, the heterocyclic compound undergoes iodination. Subsequently, a photochemically driven cross-coupling reaction between the resulting heteroaryl iodide (from **27**, **29** or **31**) and a thiol leads, respectively, to the formation of azaindoles **28**, quinolines **30** and isoquinolines **32**. For example, in the transformation aiming at isoquinoline formation, the reaction mechanism suggests that a halogen-bonding complex **33**, formed between the heteroaryl iodide and the thiolate anion, serves as the precursor for cross-coupling. Photoinduced fragmentation of this complex generates radicals **34** and **19**, which recombine to produce in this case the thioether **32**.



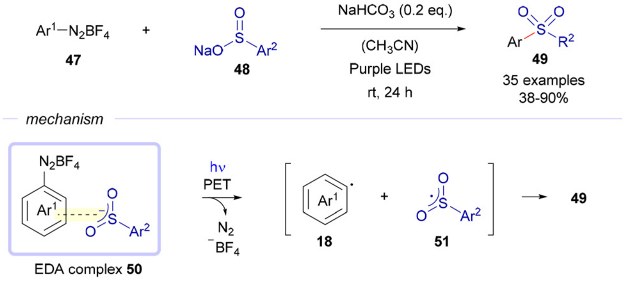
Scheme 5 One-pot strategy for the direct synthesis of heteroaryl thioethers *via* iodination followed by C–S bond formation. TBHP: *tert*-butylhydroperoxide.

Following the previous work, a different C–S cross-coupling strategy for the synthesis of different thiochromanes *via* photoinduced electron transfer was also reported by the same research group (Scheme 6).[21] In this approach, 2-iodochalcones **35** were combined with potassium ethyl xanthate **36** to form the HaB complex **42**. Upon photoexcitation with visible light, the HaB complex underwent electron transfer and fragmentation, generating radical species **43** and **44**. The rapid recombination of these radicals resulted in the formation of carbonodithiolate **45**. This intermediate then decomposed, facilitated by an additional molecule of potassium ethyl xanthate, producing a new thiolate **46**, which subsequently transformed into thiochromane **37** through an intramolecular Michael addition. Using a similar pathway, a three-component reaction involving *o*-iodobenzaldehydes **38**, sodium ethyl xanthate, and α,β-unsaturated carbonyls **39** led to the formation of thiochromenes **40** and thiochromanols **41**. In these processes, the thiolate intermediate, generated *via* the HaB-photochemically activated reaction, underwent a sequence of intermolecular Michael addition and intramolecular aldol reaction, yielding the condensed heterocyclic products **40** or **41**.

Again in 2021, Xia and Wang reported a C–S bond forming reaction *via* photochemical excitation of EDA complexes formed between aryl diazonium salts **47** and sulfinate salts **48** (Scheme 7).[22] In this case, the light-driven excitation of the



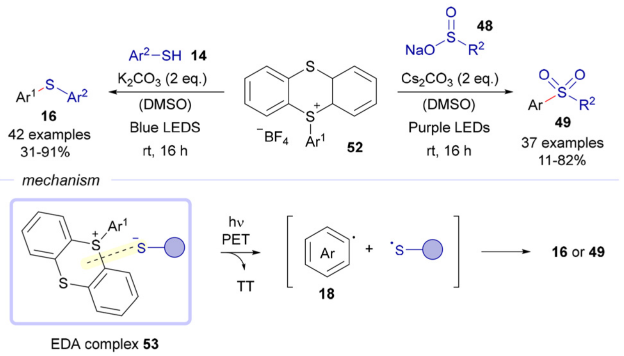
Scheme 6 Photochemical synthesis of compounds **37**, **40** and **41** *via* activation of halogen-bonding complexes.



Scheme 7 Sulfonylation transformations of aryl diazonium salts **47** *via* light-driven excitation of EDA complexes **50**.

EDA complex **50** affords the formation of the aryl radical **18** and the ambidentate sulfonyl radical **51**, which rapidly recombine to create the aryl sulfones **49**. It is important to highlight the novel role of diazonium salts as electron acceptors in this kind of photochemical transformations oriented to C–S bond formation.

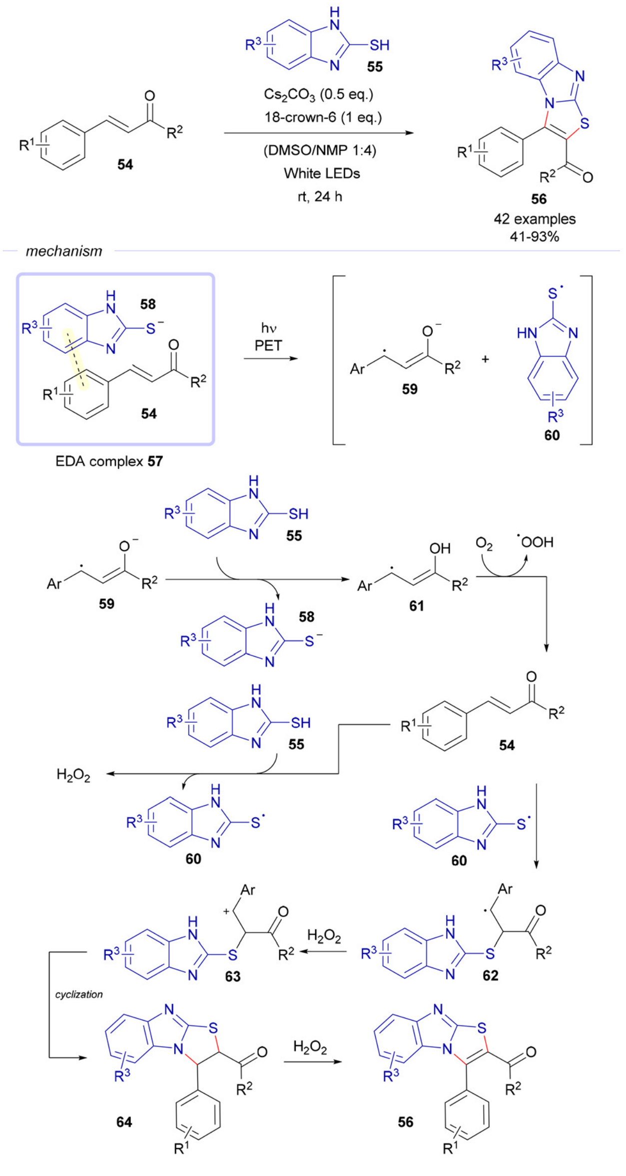
Alternatively, in 2022, Molander and co-workers demonstrated the use of aryl thianthrenium salts as electron acceptors for C–S bond formation *via* photochemical excitation of EDA complexes (Scheme 8). That same year, the same group reported a cross-coupling strategy involving thiophenols **14** or sulfinate salts **48**, which act as nucleophilic electron donors, with aryl thianthrenium salts **52** to synthesize aryl thioethers **16**,[23] and sulfones **49**,[24] respectively. Mechanistically, the reaction is initiated by light-driven excitation of the EDA complex **53**. Photoinduced electron transfer followed by fragmentation generates aryl-centered radical **18** and the corresponding sulfur-centered radical, with thianthrene (TT) forming as a byproduct in stoichiometric amounts. The recombination of these radical intermediates yields the final products, either aryl thioethers **16** or sulfones **49**, depending on the sulfur donor employed. Given the significance of thianthrenium salts as electron acceptors in photochemical processes,[25] these transformations mark an important milestone in C–S bond formation *via* this strategy. Noticeable, starting from the same reaction precursors, the same year the group of Zhang reported an application of this transformation to the preparation of bioactive and DNA-encoded molecules.[26]



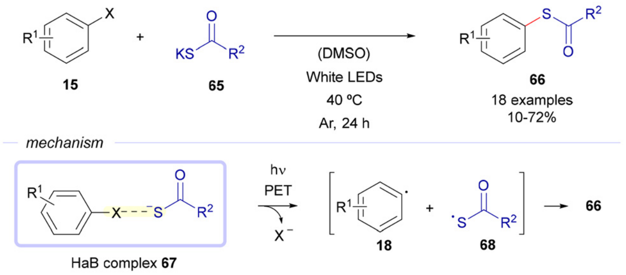
Scheme 8 Thioetherification and sulfonylation reactions of thianthrenium salts **52** *via* EDA complex photochemistry.

In 2022, Liu and co-workers developed a [3 + 2] cyclization reaction between chalcones **54** and 2-mercaptobenzoimidazoles **55** under basic conditions for the preparation of imidazo[2,1-*b*]thiazoles **56** (Scheme 9).[27] In the presence of Cs_2CO_3, 2-mercaptobenzimidazole generates the corresponding thiol anion intermediate **58**. Chalcone **54** subsequently reacts with this anionic intermediate, forming an EDA complex **57**. Upon exposure to visible light, the EDA complex undergoes an intermolecular single electron transfer, resulting in radical intermediate **60** and radical anion species **59**. The radical anion **59** then reacts with compound **55**, yielding radical **61** and regenerating intermediate **60**. Radical **61** is quenched by O_2, forming **54**. At the same time, the peroxyradical released in this step abstracts a hydrogen from **55**, generating H_2O_2 and radical **60**. Afterwards, radical intermediate **60** attacks compound **54** to produce the benzylic radical **62**. This radical **62** is subsequently transformed into the cationic intermediate **63** through the action of H_2O_2. Finally, cationic intermediate **63** undergoes nucleophilic cyclization to form intermediate **64**, which is aromatized to yield the desired products **56**.

The same year, Bugaenko and Karchava reported a simple procedure for the thioesterification of aryl halides **15** with potassium thiocarboxylates **65** under photochemical conditions



Scheme 9 Synthesis of imidazothiazoles **56** *via* EDA complex photochemistry.



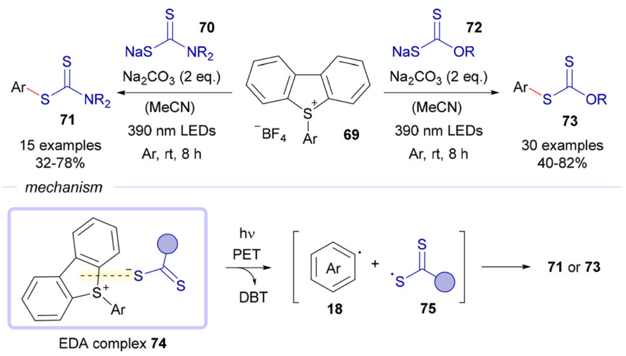
Scheme 10 Light-driven thioesterification reactions of aryl halides **15** with potassium thiocarboxylate salts **65**.

(Scheme 10).[28] Mechanistically, the transformation is initiated by the formation of an EDA complex **67** between both reaction starting materials **15** and **65**. This aggregate undergoes light-driven fragmentation into the radical species **18** and **68**, which subsequently recombine to afford the thioesters **66**. It should be noted that in 2024, the group of Sharma reported a similar transformation, in which instead of aryl halides, aryl thianthrenium salts were employed as electron acceptors.[29]

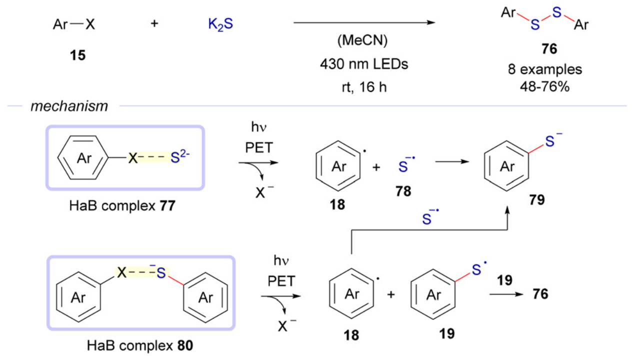
It should be noted that, very recently, the group of Liu reported a similar reaction for thioesterification based on EDA complex formation with thioester salts, but this time employing thianthrenium salts as electron acceptors.[30] Since the reaction proceeds in a similar way to the thioesterification reported by Bugaenko and Karchava, a detail discussion will be omitted.

Again in 2022, Wang and Wang reported a visible-light-driven protocol for the preparation of aryl xanthates **71** and aryl dithiocarbamates **73** through the reaction of dibenzothiophenium salts **69** with either sodium xanthogenates **70** or dithiocarbamates **72**, respectively (Scheme 11).[31] These salts are synthesized through the reaction of either alcohols or amines with CS$_2$ in basic media. The reaction is started in both cases by the formation of an EDA complex **74** between the electron acceptor part **69** and the corresponding nucleophilic sulfur source. Photoexcitation of this aggregate leads to the intermolecular SET event responsible for the fragmentation of the complex, creating the aryl radical **18** and the sulfur-centered radical **75**, along with stoichiometric amounts of dibenzothiophene (DBT). The radical intermediates recombine to afford, depending on the specific reaction, either **71** or **73** as the final products.

In 2022, Guo and Chen reported more progress in this field with the development of a novel method for synthesizing aryl disulfides. Their approach involved the use of aryl halides **15** and potassium sulfide, employing an EDA complex-mediated strategy (Scheme 12).[32] Notably, while their method is also applicable to the preparation of aryl thioethers, this aspect is beyond the scope of this review as it requires the use of a photocatalyst. The transformation begins with the formation of an EDA complex **77** between the aryl halide and the nucleophilic sulfur anion S^{2-}. Visible-light-driven fragmentation of the complex then occurs to create the aryl radical **18** and the sulfur radical anion **78**. A radical recombination of these two



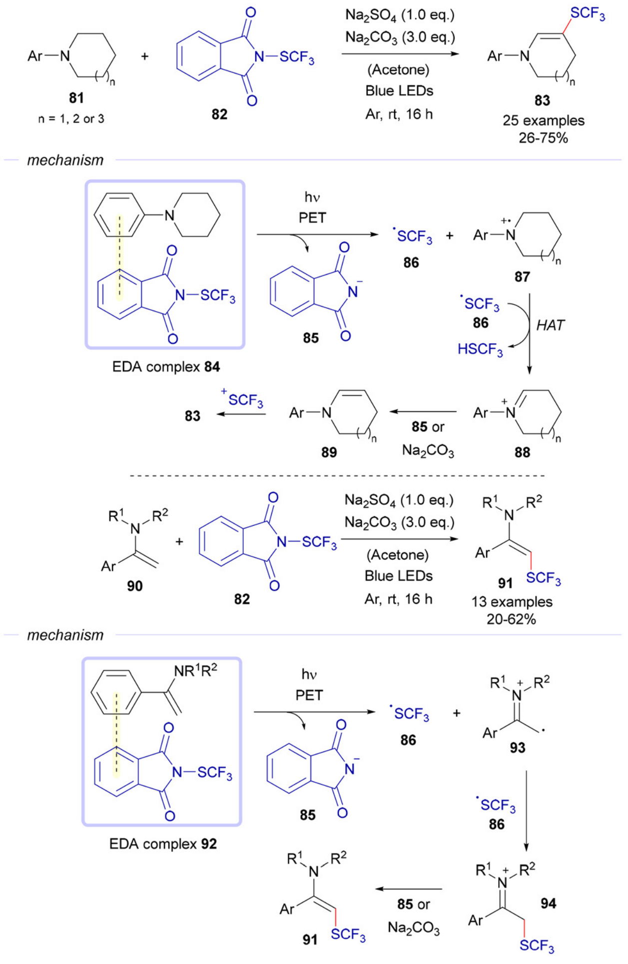
Scheme 11 Synthesis of aryl xanthates **71** and dithiocarbamates **73** driven by visible light through the EDA complex **74**.



Scheme 12 Construction of C–S bonds using inorganic sulfur salts and aryl halides *via* photoinduced activation of EDA complexes.

species leads to the formation of a sulfur thiophenolate **79**, which forms a different EDA complex **80** with another molecule of the aryl halide **15**. Again, at the specific irradiation wavelength of the reaction, a photochemical fragmentation into the corresponding aryl radical **18** and sulfur-centered radical **19** takes place. The first radical recombines with the intermediate **78** to ensure the formation of another equivalent of the aryl thiphenolate **79**, while radical recombination of two different units of **19** create the final products of the reaction, the aryl disulfides **76**.

In 2023, Xia and Wang reported a β-trifluoromethylthiolation reaction of tertiary amines **81** and enamines **90** using *N*-trifluoromethylthiophthalimide **82**.[33] Since these reactions follow distinct pathways, each transformation is presented separately in Scheme 13. For the trifluoromethylthiolation of amines **81**, the process begins with the photochemical activation of the EDA complex **84**, leading to its fragmentation into a phthalimide anion **85**, a trifluoromethylthio radical **86**, and an amine radical cation **87**. The latter undergoes hydrogen atom abstraction by radical **86**, generating the iminium species **88**. Subsequent deprotonation of **88** by either **85** or sodium carbonate produces an enamine intermediate **89**, which then reacts with the electrophilic trifluoromethylthiophthalimide **82** to yield the final products **83**. In the case of the trifluoromethylthiolation of enamines **90**, the reaction proceeds through the formation of an EDA complex **92**. Upon light-driven excitation, this complex dissociates into the phthalimide anion **85**, the trifluoromethylthio radical **86**, and a radical cation intermediate **93**. Radical recombination between **93** and **86** generates the iminium cation **94**, which undergoes base-mediated deprotonation by either **85** or sodium carbonate to afford the final products **91**.

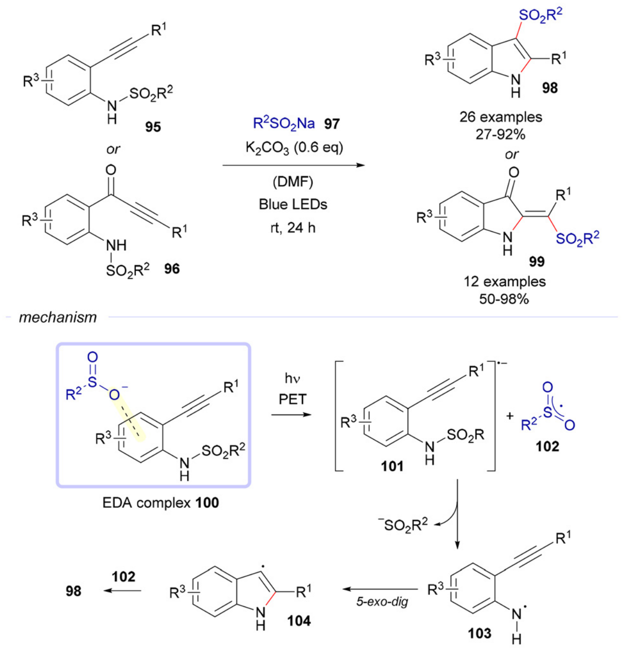


Scheme 13 Photochemical trifluoromethylthiolation reactions of tertiary amines **81** and enamines **90**. HAT: hydrogen atom transfer.

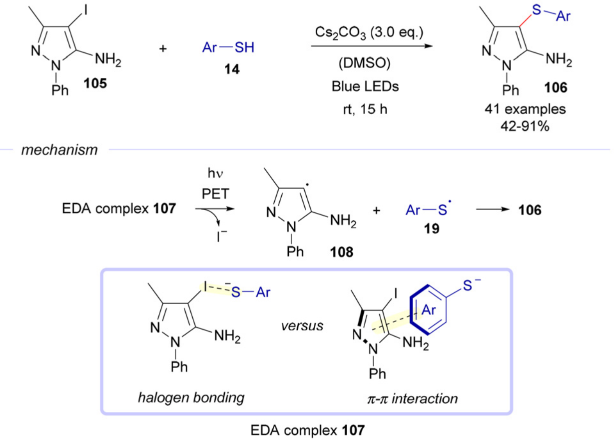
In 2024, Hu and Xu reported a cyclization reaction of alkynes to furnish 3-sulfonylindoles **98** and vinyl sulfone oxindoles **99**, depending on which starting material, **95** or **96**, respectively, was used in combination with a sodium sulfinate **97** (Scheme 14).[34] In order to illustrate the mechanism of this transformation, the case of the synthesis of compounds **98** will be contemplated. In this case, the corresponding sodium sulfinate reacts with the starting material **95** in the presence of K_2CO_3 to form an EDA complex **100**. Under light exposure, the EDA complex undergoes an intermolecular single electron transfer process from the donor **97** to the acceptor **95**, leading to the generation of a sulfonyl radical **102** and an *N*-sulfonamide radical anion **101**. The fragmentation of radical anion **101** yields a sulfonyl anion and an *N*-centered radical intermediate **103**. A 5-*exo-dig* cyclization of intermediate **103** results in the formation of an indole radical intermediate **104**. Subsequently, intermediate **104** and sulfonyl radical **102** undergo selective radical–radical coupling to produce the target compound **98**.

Also in 2024, the group of Ramesh reported an EDA-complex-mediated photochemical thioetherification reaction of halogenated pyrazole-5-amines **105** with thiophenols **14** under basic conditions (Scheme 15).[35]

Mechanistically, the reaction is believed to proceed through the formation of an EDA complex **107** between the deprotonated thiophenol and the electron acceptor, the corresponding compound **105**. The attractive force that is responsible for the creation of such aggregate could be due to halogen-bonding and/or π–π interactions. Subsequent light-driven fragmenta-



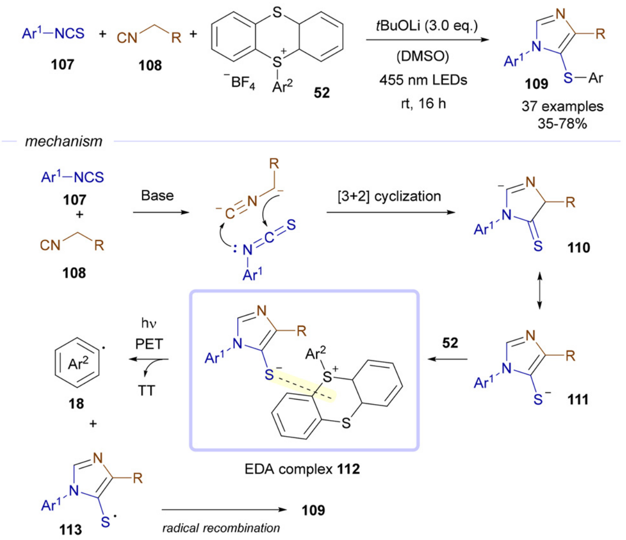
Scheme 14 EDA complex-facilitated cascade cyclization of alkynes for the synthesis of 3-sulfonylindoles **98** and vinyl sulfone oxindoles **99**.



Scheme 15 Photochemical synthesis of thiolated pyrazole-5-amines **106** *via* formation of EDA complexes.

tion of the complex leads to the formation of two different radical intermediates: a carbon-centered radical **108** and a sulfur-centered radical **19**. An eventual radical recombination step grants the creation of the final sulfurated heterocycles **106**.

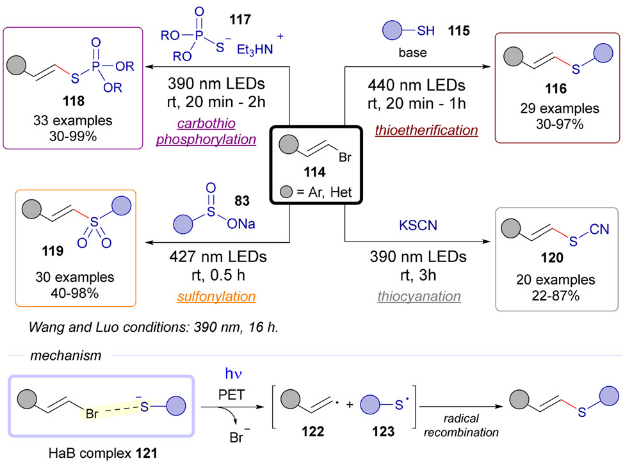
In 2024, Yang and co-workers reported a one-pot multicomponent reaction which makes use of isothiocyanates **107**, isocyanides **108**, and thianthrenium salt-functionalized arenes **52** to access trisubstituted imidazoles **109** (Scheme 16).[36] The transformation is started by the base-mediated deprotonation of isocyanides **108**, which initially undergo a [3 + 2] cycloaddition with aryl isothiocyanates **107**, resulting in the for-



Scheme 16 One-pot multicomponent reaction of isothiocyanates **107**, isocyanides **108**, and thianthrenium salts **52** to prepare trisubstituted imidazoles **109**.

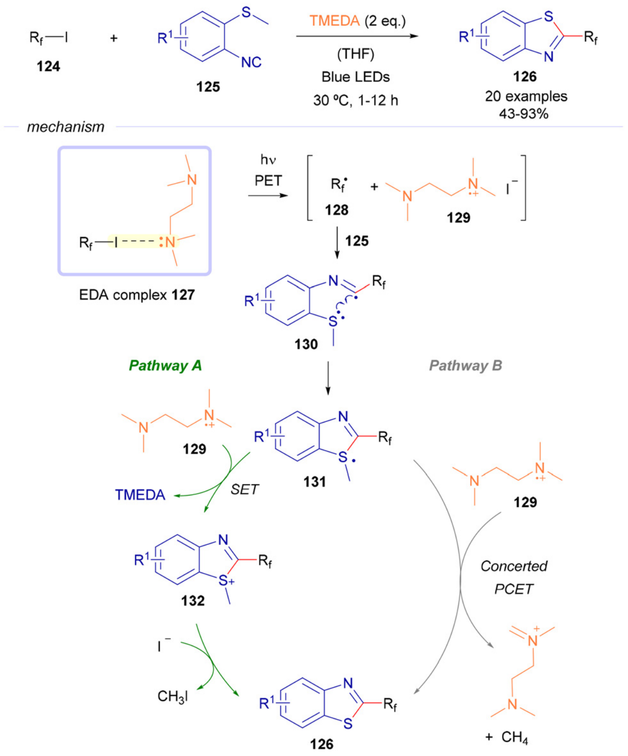
mation of intermediate **110**. Through tautomerism, sulfur anions **111** are generated, which can behave as electron donors. These anions then form an EDA complex **112** in solution with thianthrenium salts **52**. Upon exposure to visible light, the ground-state EDA complex transitions to its excited state, triggering an intermolecular single electron transfer from sulfur anions **111** to thianthrenium salts **52**. This leads to the release of thianthrene and the formation of an aryl radical **18** along with a thiyl radical **113**. Finally, a radical coupling between **18** and **113** produces the target products **109**.

In the realm of C(sp^2)–S bond-forming reactions, our research group has pioneered synthetic methodologies leveraging the generation of highly reactive alkenyl radicals. Our approach employs alkenyl halides as starting materials, which serve as the electron acceptor component in EDA complexes, specifically those stabilized by halogen-bonding interactions. Various nucleophilic sulfur-based species (including thiols **115**, phosphorothioate diester salts **117**, sulfinates **83**, and thiocyanate salts) are utilized to enable streamlined thioetherifications,[37] carbothiophosphorylations,[38] sulfonylations,[39] and thiocyanations,[40] respectively. In parallel to the development by our group of the sulfonylation reaction, the group of Wang and Luo developed a transformation starting from the same reaction precursors, alkenyl bromides **114** and sulfinate salts **83**.[41] However, different reaction conditions (irradiation from 390 nm LEDs, 16 h) to ours (427 nm LEDs, 0.5 h) were reported. All in all, these transformations are distinguished by their remarkable functional group tolerance, high stereoselectivity, operational simplicity, and scalability. Detailed mechanistic investigations were conducted to confirm both the radical nature of the process and the role of the halogen-bonding EDA complex as the initiator. Under visible light, the fragmentation of the corresponding HaB complex **121** gener-



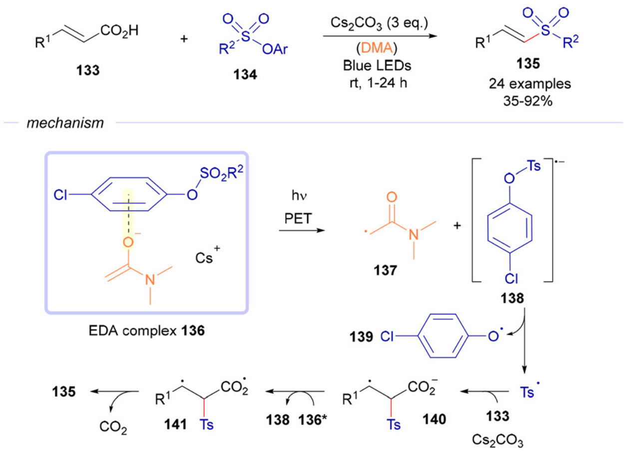
Scheme 17 Thioetherifications, carbothiophosphorylation, sulfonylation and thiocyanation reactions of alkenyl bromides **114** based on photochemical activation of HaB complexes.

ates an alkenyl radical **122** and a sulfur-centered radical **123**. Subsequent radical recombination of these intermediates culminates in the formation of the specific C(sp^2)–S bond in each of the described transformations in Scheme 17.



Scheme 18 Synthesis of 2-perfluoroalkylbenzothiazoles **126** based on the employment of TMEDA as the sacrificial donor.

2.2.2. **Activation of the electron acceptor with a sacrificial donor.** One of the first works reported for photochemical activation of HaB complexes using a sacrificial electron donor was reported in 2019 by Chen and Yu. In this work a perfluoroalkylation/cyclization approach for synthesizing 2-perfluoroalkylbenzothiazoles **126** through the photoinduced formation of perfluoroalkyl radicals **128** (Scheme 18).[42] In this process, tetramethylethylendiamine (TMEDA) was employed as a halogen-bond donor to facilitate the generation of radicals **128** and **129** through the photochemical fragmentation of EDA complex **127**. When *o*-methylthioisocyanide **125** is present, the radical **128** reacts with the isocyanide to form a new radical intermediate **130**, which undergoes rapid intramolecular cyclization to create the benzothiazole framework of **126**, creating a sulfur-centered radical **131**. From this point, the reaction likely proceeds *via* two distinct pathways. In Pathway A, radical intermediate **131** is oxidized by the radical cation **129**, regenerating TMEDA and forming a sulfonium cation **132**. A subsequent nucleophilic attack by I^- on the methyl group of intermediate **132** yields the final benzothiazole **126**, with MeI generated as a byproduct. The methyl iodide then reacts with TMEDA, producing the corresponding quaternary ammonium salt. Alternatively, pathway B involves a proton-coupled electron transfer (PCET) event between **131** and **129**, which directly produces the target compound **126** alongside methane and a cationic imine salt of TMEDA as byproducts. The quantum yield of the reaction (φ = 0.2) was measured, ruling out the possibility of a radical chain propagation mechanism.



Scheme 19 Preparation of alkenyl sulfones **135** through the initial formation of an EDA complex **136** between **134** and DMA.

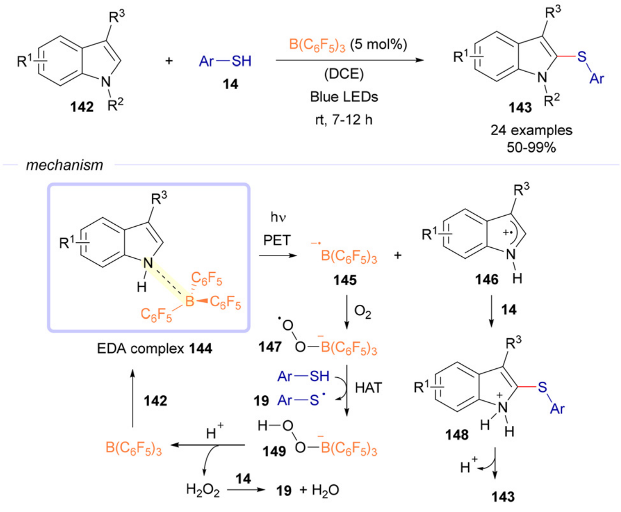
Also the same year, in 2019, Quian and Xuan reported a decarboxylative sulfonylation of cinnamic acids based on light-driven activation of EDA complexes.[43] A conceivable reaction pathway is illustrated in Scheme 19. Initially, EDA complex **136** was generated through the interaction between an aryl sulfonate phenol ester **134** and dimethylacetamide (DMA) in the presence of Cs_2CO_3. Exposure to visible light activated the complex (**136***), which then underwent single-electron transfer, yielding radical anion species **138** alongside a carbon-centered radical intermediate, **137**. The subsequent fragmentation of **136** released a tosyl radical, which reacted with the double bond of the cinnamic acid to form a benzyl radical, **140**.

Oxidation of benzyl radical **140** by the excited complex **136*** led to the formation of intermediate **141** while regenerating radical anion **138**. Finally, **141** underwent decarboxylation, resulting in the formation of the desired vinyl sulfone product **135**.

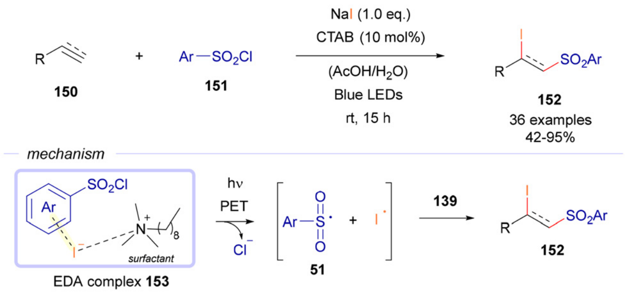
In 2022, three years later, Huang and Zhang reported a comparable transformation to the one previously described, substituting cinnamic acids with alkynes to achieve an oxosulfonylation reaction.[44] Given the similarity in the reaction mechanism to the one discussed earlier, a detailed mechanistic explanation will not be included here.

Interestingly, the group of Tang reported in 2021 a photochemical reaction *via* EDA complexes where catalytic amounts of the sacrificial donor were used.[45] This new activation mode within the EDA complex photochemistry was used for the cross-coupling between indoles **142** and thiophenols **14** to furnish the final products **143**, where $B(C_6F_5)_3$ served as a catalyst to facilitate such process (Scheme 20). Mechanistically, the process begins with the formation of an EDA complex **144** between indole **142** and $B(C_6F_5)_3$. Upon exposure to visible light, a single-electron transfer takes place within the EDA complex, leading to the creation of a radical anion **145** and a radical cation **146**. Intermediate **145** reacts with oxygen to form the oxygenated intermediate **147**, which abstracts a hydrogen atom from **14** to produce intermediate **149** and a sulfur-centered radical. Protonation of complex **149** results in the formation of hydrogen peroxide, and $B(C_6F_5)_3$ is regenerated, completing the catalytic cycle. Hydrogen peroxide oxidizes **14** and can also generate sulfur radical **19** along with water. Intermediate **146** interacts with **19** to yield intermediate **148**, which is subsequently deprotonated to produce the final product **143**. All in all, this approach introduces a novel reaction framework that employs $B(C_6F_5)_3$ as a single-electron oxidant.

In 2021, Li and co-workers developed a novel strategy for C–S bond formation utilizing the photochemistry of EDA complexes in the presence of surfactants (Scheme 21).[46] The method enabled the preparation of alkenyl or alkyl sulfones **152** by combining sulfonyl chlorides **151**, NaI, catalytic amounts of cetyltrimethylammonium bromide (CTAB) as a surfactant, and alkenes or alkynes **150** as radical trapping agents. Mechanistically, the reaction proceeds *via* the formation of an EDA complex **153** in water, where the aromatic sulfonyl chloride acts as the electron acceptor and iodide serves as a sacrificial donor for photochemical activation. The surfactant assists in the assembly of the EDA complex **153** *via* encapsulation of the different starting materials. Upon irradiation with blue light, the EDA complex undergoes fragmentation, generating two distinct radical species, **51** and I^-. These radicals are subsequently intercepted by the alkenes or alkynes, resulting in a 1,2-difunctionalization of the unsaturation and yielding the final sulfone products **152**.

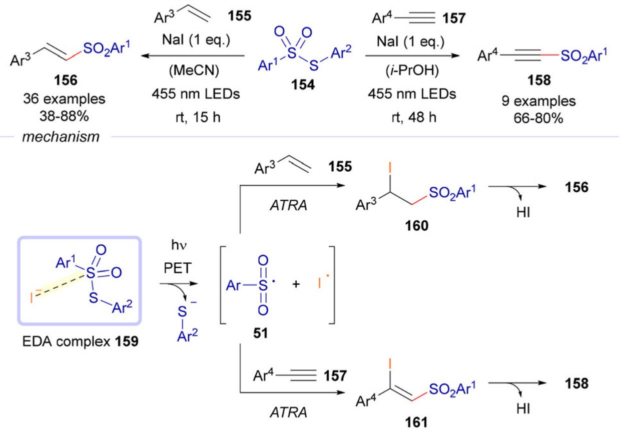


Scheme 20 Photochemical C–S bond forming reactions between indoles **142** and thiols **14** catalyzed by $B(C_6F_5)_3$.



Scheme 21 Assistance of surfactants in EDA complex formation for the preparation of sulfones **152** from sulfonyl chlorides **151**, NaI and alkenes/alkynes.

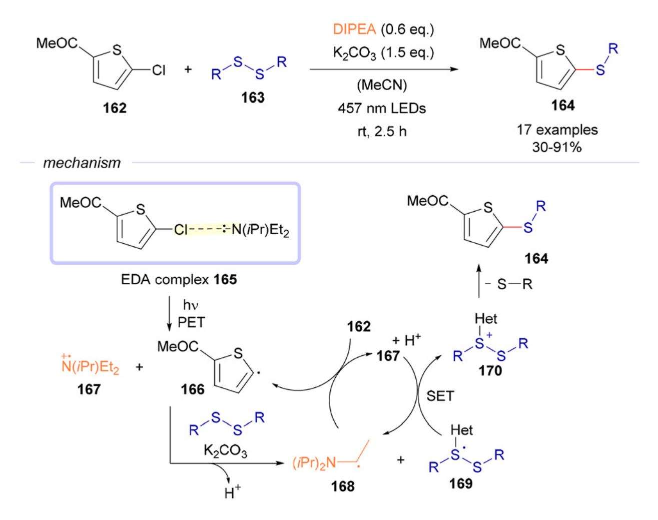
The assistance of sodium iodide as a sacrifical electron donor in EDA complex photochemistry oriented to C–S bond formation was also exploited by the group of Jiang and Li to carry out sulfonylation reactions of alkenes **155** or alkynes **157**, rendering respectively alkenyl sulfones **156** or alkynyl sulfones **158** (Scheme 22).[47] In these reactions, thiosulfonates **154** were employed as the electrophilic species responsible for the for-



Scheme 22 Synthesis of alkenyl or alkynyl sulfones by visible light through an EDA complex **159** with assistance of NaI.

mation of the EDA complex **159** with sodium iodide. Photochemical excitation of the aggregate creates the sulfonyl radical **51** and iodide radical intermediates. Then, depending on the radical-trapping agent, two different transformations can occur based on an atom transfer radical addition process. In the radical intermediates are intercepted with alkenes **155**, a new intermediate **160** is formed, which upon elimination of HI forges the alkenyl sulfones **156**. On the other hand, if alkynes are used, the intermediate **161** is created, which also can undergo elimination of HI to furnish the corresponding alkynyl sulfones **158.** It should be noted that in this last case, due to the elimination step, overall, a C(sp)–S bond is formed in the transformation to forge compounds **158**.

In 2023, the group of Mancheño reported a visible-light driven thiolation reaction of 2-chlorothiophenes **162** employing disulfides **163** as the sulfur source (Scheme 23).[48] The mechanism of this transformation is believed to proceed through the generation of the EDA complex **165**, formed between the 2-cholothiophene (electron acceptor) and the diisopropylethylamine (DIPEA, sacrificial electron donor). Photochemical excitation of this complex forms the corresponding radical cation amine **167** and the carbon-centered radical **166**, which arises from the reduction of the C–X bond. At this point, the first radical intermediate is deprotonated with the assistance of potassium carbonate, and reacts with the starting disulfide **163** to form a new carbon-centered radical **168** and a sulfur-centered radical **169**. Intermediate **168** is believed to start a radical chain propagation through its reaction with another equivalent of **162**, generating in this way an additional equivalent of the radical intermediate **166** and **167**. At this point, **167** undergoes a single electron transfer event with **169**, generating the sulfur-centered cationic species **170** and an equivalent of **168**. Intermediate **170** undergoes fragmentation, eliminating a thiophenolate anion and generating the final products of the reaction **164**. The existence of this radical chain propagation mechanism is supported by the quantum yield measurement ($\phi = 4$).



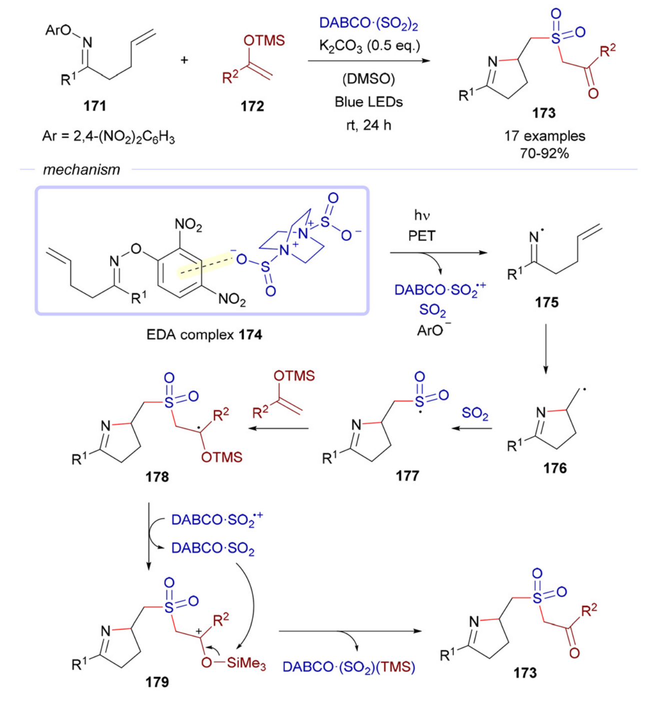
Scheme 23 Photoactivation of alkylamine-based EDA complexes for the thiolation of 2-chlorothiophenes **162**.

In summary, this section highlights how photochemical activation of EDA complexes serves as a powerful strategy for C(sp^2)–S bond construction. To date, the developed methodologies incorporate a variety of electron acceptor molecules (primarily organic halides and sulfonium salts) paired with nucleophilic electron donors, typically sulfur-centered anionic species such as thiolates or sulfinates. Alternatively, the use of sacrificial agents (*e.g.*, amines, enolates, or iodide anions) in combination with sulfur sources has also been demonstrated as an effective approach for C(sp^2)–S bond formation within EDA complex photochemistry.

2.3. C(sp^3)–S bond forming reactions

In addition to the significant progress made in the photochemical construction of C(sp^2)–S bonds, substantial advancements have also been achieved in analogous methodologies for forming C(sp^3)–S bonds. As in the previous section, the following subsections will be organized based on the type of photochemical transformation.

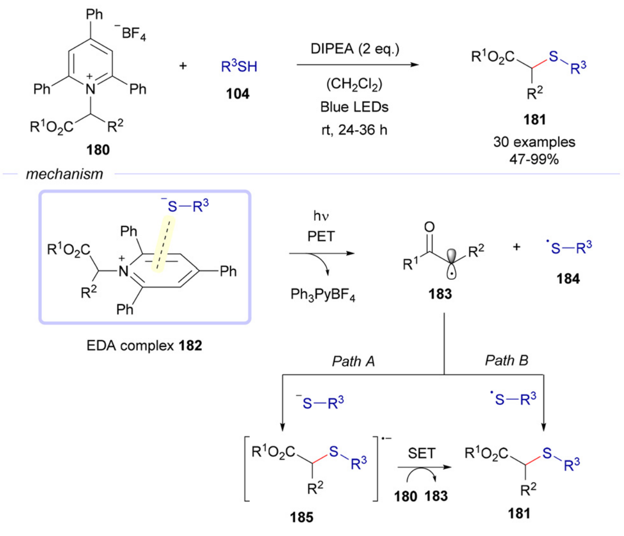
2.3.1. Nucleophilic sulfur source as the electron donor. One of the first examples on C(sp^3)–S bond-forming reactions *via* light-driven excitation of EDA complexes was reported by the group of Wu in 2017 (Scheme 24).[49] This works consists of a *N*-centered radical initiated cascade reaction for the construction of 3,4-dihydro-2*H*-1,4-thiazine-1,1-dioxides **173** from 4-diazabi-cyclo[2.2.2]octane disulfate [DABCO·$(SO_2)_2$], oximes **171** and silyl enol ethers **172**. The transformation starts with



Scheme 24 Photochemical cascade reactions for the construction of 3,4-dihydro-2*H*-1,4-thiazine-1,1-dioxides **173**. TMS: trimethylsilyl.

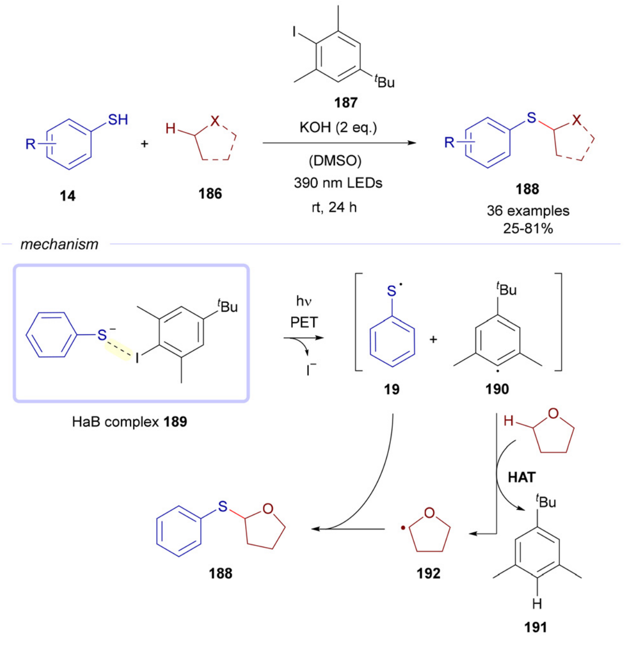
the formation of an EDA complex **174** between [DABCO·$(SO_2)_2$] and the corresponding oxime **171**, which presents an accentuated electron acceptor character due to the electron-poor nature of the aromatic core linked to the nitrogen. Photoinduced electron transfer causes the fragmentation of this complex into several molecules: sulfur dioxide, the radical cation from DABCO·(SO_2), the corresponding phenoxide and the nitrogen-centered radical **175**. At this point, an intramolecular 5-*exo-trig* cyclization renders the formation of a new radical species **176**. This intermediate captures sulfur dioxide, generating a new sulfur-centered radical **177**, which adds onto the silyl enol ether **172** to create intermediate **178**. At this point, this radical intermediate is oxidized by the radical cation from DABCO·(SO_2), generating the carbocationic species **179**. Eventually, abstraction of the silyl residue facilitated by DABCO·(SO_2) generates the final products **173**, alongside with an equivalent of DABCO·(SO_2)(TMS).

In 2019, the group of Liao reported a thioetherification reaction aiming at the formation of C(sp^3)–S bonds *via* EDA complex photochemistry (Scheme 25).[50] In this case, Katriztky salts **180** were used as electron acceptors in combination with different thiols **104**, seeking the formation of an EDA complex **182** between both reactants to carry on a thioetherification transformation. Fragmentation of this complex upon exposure to blue light drives the formation of two different radical species, **183** and **184**, along with the elimination of a pyridinium salt as a byproduct of the reaction. At this point two different paths are proposed to explain the formation of the final products of the reaction **181**. Path A consists of a recombination of the carbon-centered radical **183** with an equivalent of the corresponding thiolate anion, resulting in the creation of a radical anion **185**. This species reduces a different molecule of the starting material **180** through a single electron transfer, generating an additional equivalent of the radical intermediate **183** along with the thioether **181**. Path B shows the direct recombination of the radical species **183** and **184** to forge the thioethers **181**. To the best of our knowledge, this is one of the first examples in which Katritzky salts were used as electron acceptors in C–S bond forming reactions driven by the formation of EDA complexes.[51]

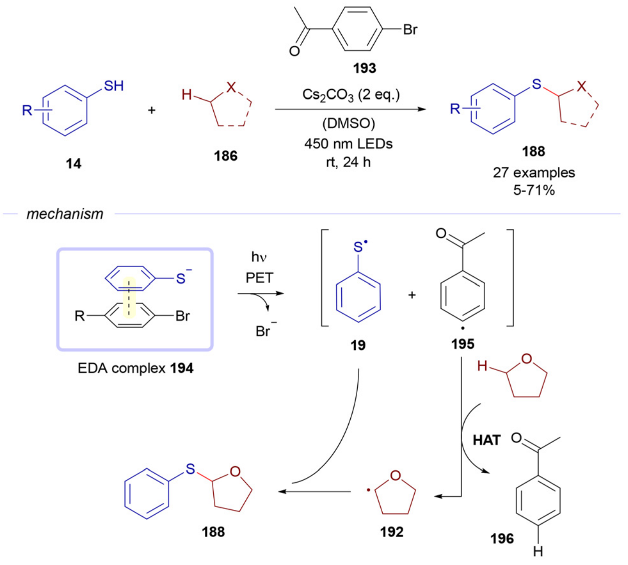


Scheme 25 Thioetherification reactions of Katriztky salts **180** through the formation of EDA complexes **182**.

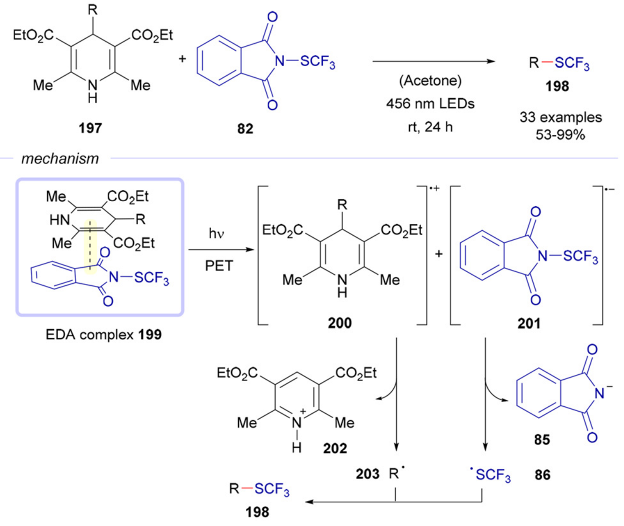
In 2021, both Akayima's and Xia's research groups independently developed comparable photochemical methods for activating C(sp^3)–H bonds in the synthesis of sulfides. Xia and coworkers specifically explored the thiolation of etheric, benzylic, and allylic substrates **186** using thiophenols **14** (Scheme 26).[52] Their approach involved the photochemical excitation of the halogen-bonding complex **189**. In this study, 2,6-dimethyl iodobenzene **187** serves as the electron acceptor. Upon exposure to light, the typical sequence of photoexcitation, PET, and fragmentation produces radicals **19** and **190**. Due to the steric hindrance of the 2,6-disubstituted iodide, direct radical recombination is prevented. Instead, the phenyl radical **190** abstracts a hydrogen atom from the Csp^3–H bond of substrate **186**, which is present in excess, leading to the formation of the Csp^3-centered radical **192**. This radical then recombines with the thiyl radical **19**, yielding thioethers **188** in moderate to good yields. In contrast, Akayima's research proposes that the transformation is initiated by an EDA complex **194** between 4-bromoacetophenone **193** and an aromatic thiolate **14** (Scheme 27).[53] Unlike Xia's study, no HaB complex was considered in this case. Instead, the authors noted that the reaction does not occur with alkanethiols, highlighting the crucial role of π–π stacking interactions in the EDA complex **194**. In this case, photochemical excitation of the aggregate **194** leads to the formation of the radical species **19** and **195**. The carbon-centered radical intermediate **195** abstracts a hydrogen from



Scheme 26 Xia's approach to the C(sp^3)–H bond functionalization reactions for the preparation of thioethers **188**.



Scheme 27 Akiyama's work on C(sp^3)–S bond forming transformations through the activation of C(sp^3)–H bonds.



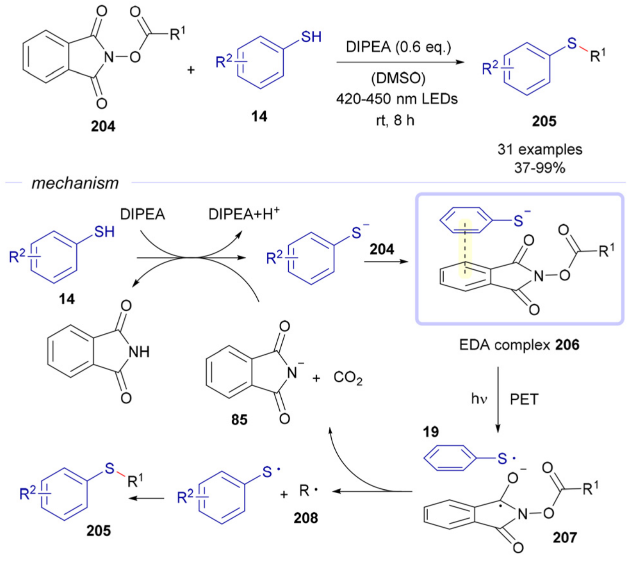
Scheme 28 Trifluoromethylthiolation reactions through photochemical activation of EDA complexes **199**.

186, forging **192** and forming **196** as a byproduct. Eventually, a radical recombination step between **192** and **19** grants the formation of the final products **188**.

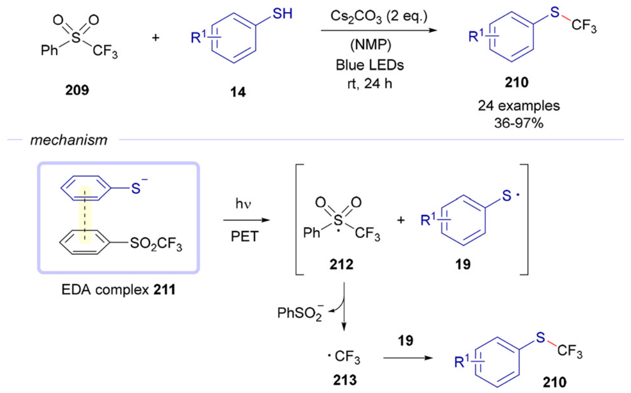
Again in 2021, the group of Molander reported a protocol for decarbonylative trifluoromethylthiolation of *via* activation of EDA complexes (Scheme 28).[54] In this study, dihidropyridines (DHPs) **197** reacted with *N*-(trifluoromethylthio)phtalimide **82** to afford he creation of trifluoromethylthiolated molecules **198**. While extensive mechanistic studies and multiple pathways are contemplated by the authors, a simplified description will be made. Interested readers are encouraged to consult the original publication for details. The reactions proceed *via* the formation of the EDA complex **199**, which light-driven fragmentation grants the creation of two different radical ion intermediates, the radical cation **200** and the radical anion **201**. Intermediate **200** decomposes into a pyridinium cation **202** and a carbon-centered radical **203**. Simultaneously, the radical anion **201** fragments into a phtalimide anion **85** and sulfur-centered radical **86** through reduction of the N–S bond. Radical recombination of intermediates **203** and **86** grant the formation of the final products **198**.

Also in 2021, the research group of Song reported a photochemical transformation which makes use of redox active esters **204** as electron acceptors for thiolation reactions with thiophenols **14** (Scheme 29).[55] When a thiolate anion is generated under basic media, the formation of an EDA complex **206** takes place, which fragmentation produces the sulfur-centered radical **19** and the radical anion **207**. Redox active esters are known to be radical precursors upon one electron reduction.[56] The corresponding radical anion **207** that is initially formed fragments into phthalimide anion **85** and the carbon-centered radical **208**. Eventually, radical recombination between **208** and **19** forges the final thioethers **205**.

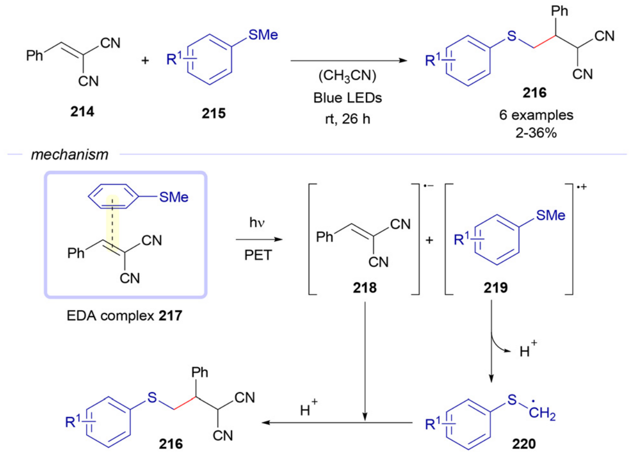
In 2022, the group of Hu developed a photochemical protocol for the *S*-trifluoromethylation of thiophenols **14** with trifluoromethyl phenyl sulfone **209** (Scheme 30).[57] The transformation is initiated by the formation of an EDA complex **211** between sulfone **209** and the corresponding thiphenolate anion from **14**, allowing for the expected formation of the sulfonyl radical **212** and sulfur-centered radical **19**. Intermediate **212** is unstable, decomposing into a trifluoromethyl radical **213** and a sulfinate anion. Radical recombination between intermediates **213** and **19** renders the desired *S*-trifluoromethylated thiophenols **210**.



Scheme 29 Visible-light-driven thioetherification reactions with redox active esters **204** and thiophenols **14**.



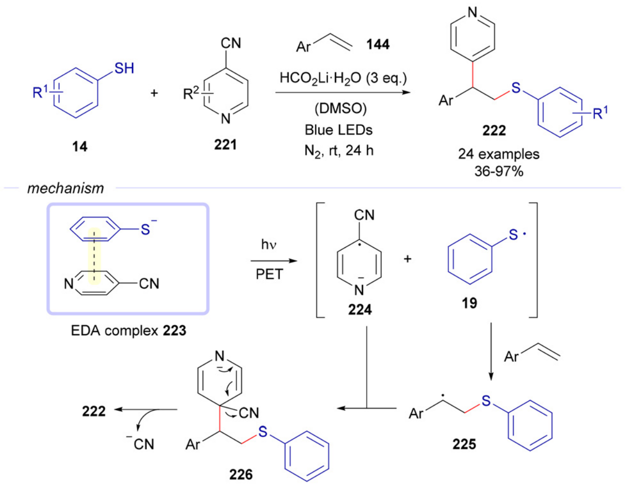
Scheme 30 Visible-light-driven trifluoromethylation of thiphenols **14** with trifluoromethyl phenyl sulfone **209**.



Scheme 31 Formation of aryl alkyl thioethers **216** by photochemical excitation of EDA complexes **217**.

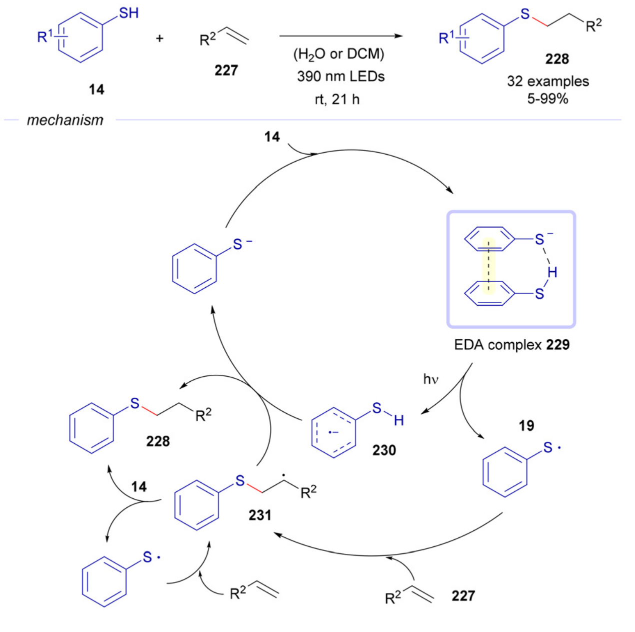
In 2023, Hitomi and co-workers discovered an EDA-complex driven transformation between benzylidenemalononitriles **214** and thioethers **215** for the construction of aryl alkyl thioethers **216** (Scheme 31).[58] Photochemical fragmentation of the EDA complex **217**, formed between both reactants, grants the formation of the radical anion **218** and the radical cation **219**. By losing a proton, intermediate **219** evolves to the carbon-centered radical **220**, which recombines with **218**. After protonation, the final products **216** are formed.

Also the same year, the group of Shen reported multicomponent transformation for the 1,2-difunctionalization of styrenes **144** with thiophenols **14** and 4-cyanopyridines **221** (Scheme 32).[59] The reaction is initiated by the deprotonation under basic conditions of the corresponding thiophenol **14**, rendering a thiophenolate anion which aggregates with compound **221** to form an EDA complex **223**. Visible-light-driven excitation of this complex causes its fragmentation into the radical anion **224** and the sulfur-centered radical **19**. The latter intermediate adds to the alkene **144**, forming an alkyl-centered radical **225**. Radical recombination between **225** and **224** creates a new intermediate **226**, in which aromatization of the pyridine core through elimination of a cyanide group forges the final products **222**. In 2024, the Shi group reported a distinct 1,2-difunctionalization of alkenes based on similar reactivity. However, their method employed an iron salt and used trifluoromethylarenes instead of 4-cyanopyridines.[60] To avoid redundancy, a detailed mechanistic discussion will not be provided.



Scheme 32 Difunctionalization reaction of styrenes **144** to create compounds **213**.

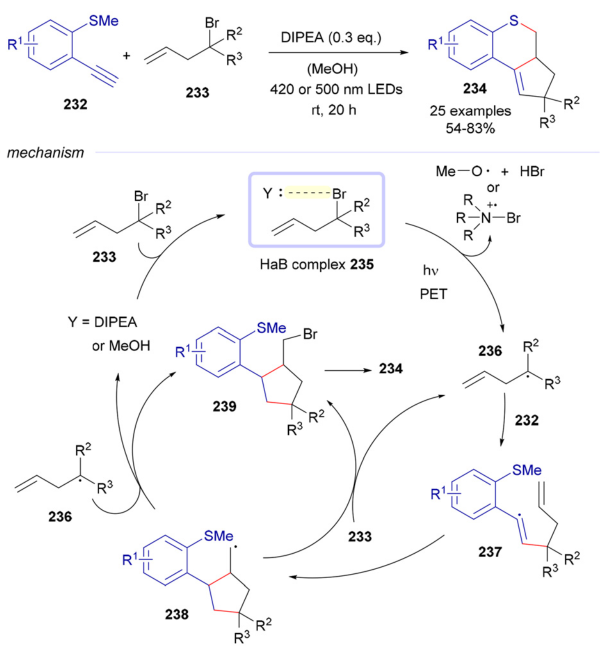
In 2023, Renzi's group reported a thiol–ene reaction between alkenes **227** and thiophenols **14**, driven by the formation of EDA complexes (Scheme 33).[61] In this process, a molecule of **14** pairs with its deprotonated form to assemble



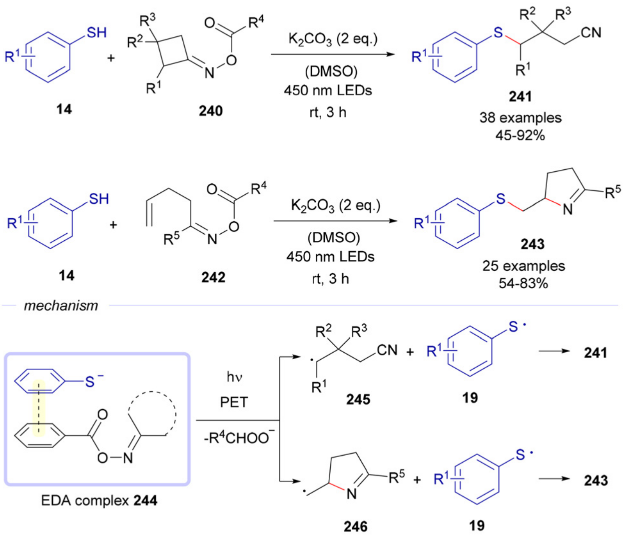
Scheme 33 Thiol–ene transformations of alkenes **227** into sulfides **228**.

an EDA complex **229**. Upon photochemical excitation, this complex generates a radical anion **230** and a sulfur-centered radical **19**, which subsequently adds to olefin **227**, forming an alkyl-centered radical **231**. This intermediate can then evolve *via* two pathways: hydrogen abstraction from radical anion **230**, yielding the final product **228** and a thiophenolate anion; or hydrogen abstraction from **14**, also forming **228** while regenerating radical **19**. It should be noted that photochemical thiol–ene and thiol–yne reactions represent a powerful method for the construction of organosulfur compounds, where also photocatalytic versions have been recently developed by the groups of König and Ananikov.[62]

In 2024, Yamaguchi and Itoh developed a photochemical halogen-bonding assisted ATRA/cyclization reaction between thioethers **232** and homoallyl bromides **233** for the construction of tricyclic heterocycles **234** (Scheme 34).[63] Initially, the halogen-bonding complex **235** forms through the interaction between **233** and either DIPEA or methanol, which act as electron donors (abbreviated as Y in Scheme 33). Upon exposure to light, this complex enters an excited state, leading to the breaking of the C–Br bond, resulting in the formation of the alkyl radical **236** along with either an ammonium radical cation or a methoxy radical. The radical **236** then undergoes an addition reaction with **232**, forming a new C–C bond and generating radical intermediate **237**. This intermediate subsequently undergoes an intramolecular radical 5-*exo-trig* cyclization, leading to the formation of radical intermediate **238**. Next, radical species **238** reacts with **236**, producing the brominated compound **239** while simultaneously regenerating the amine. Additionally, there is a possibility of a radical chain mechanism where the carbon-centered radical **238** interacts with **235**, leading to the formation of brominated compound **239** and the regeneration of **238**. Finally, the intermediate **239** formed *via* these pathways undergoes a second cyclization step, ultimately yielding the desired tricyclic compound **234**.



Scheme 34 Photochemical halogen-bonding-assisted reaction between thioethers **232** and homoallyl bromides **233** for the preparation of tricyclic heterocycles **234**.

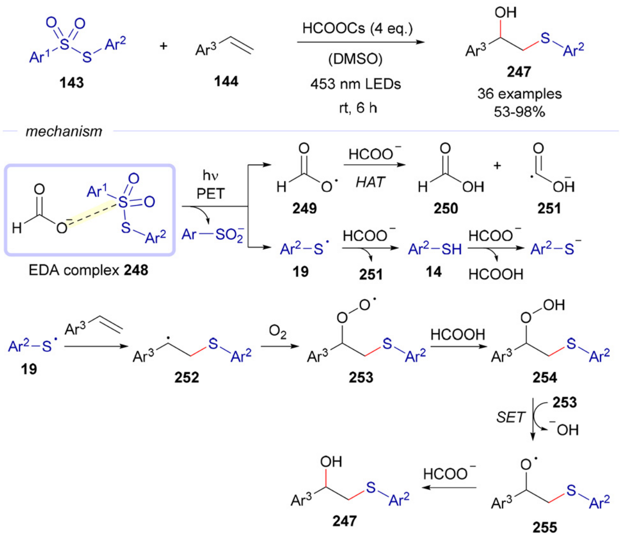


Scheme 35 Photochemical EDA-complex-mediated reactions with oxime esters to form compounds **241** and **243**.

Also in 2024, Tong and Zhong developed a visible-light-driven reaction between different oxime esters **240** or **242** and thiophenols **14** to forge either compounds **241** or **243** (Scheme 35).[64]

The reactions take place through the formation of an EDA complex **244** between both starting materials. Upon photoinduced electron transfer from the thiophenolate anion to the corresponding oxime ester, the latter is fragmentated through reduction of the N–O bond. If oximes **240** are used, a new carbon-centered radical **245** is formed, which recombines with the sulfur-centered radical **19** to forge compounds **243**. On the other hand, when oxime precursors **242** are employed, a different radical species **246** is created, which arises from a previous 5-*exo-trig* cyclization. This intermediate recombines with **19** to create the final products **243**.

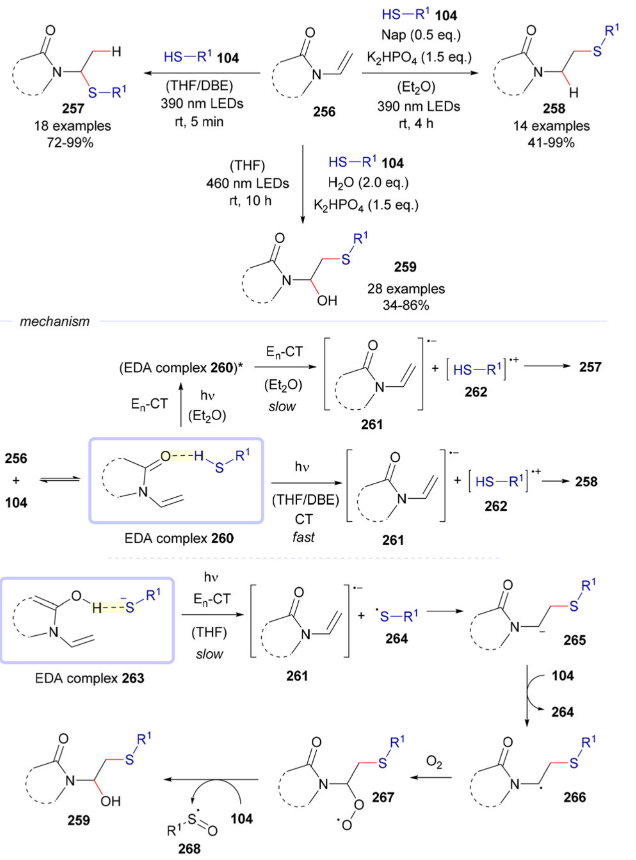
Also in 2024, Zhou and Li reported a 1,2-difunctionalization of alkenes **144** for the synthesis of β-hydroxysulfides **247** (Scheme 36).[65] The reaction begins with the formation of an EDA complex **248** between the formate anion and thiosulfone **143**. Upon photochemical fragmentation, this complex generates an oxygen-centered radical **249** and a sulfur-centered radical **19**. Intermediate **249** abstracts a hydrogen atom from another equivalent of the formate anion, yielding formic acid and radical anion species **251**. Simultaneously, radical **19** undergoes a series of hydrogen atom transfer events, ultimately reducing to the corresponding thiophenolate anion. Alternatively, radical **19** can add to olefin **144**, forming a carbon-centered radical **252**. Quenching of this intermediate by O_2 produces peroxy radical **253**, which is then converted



Scheme 36 1,2-Difunctionalization reactions of alkenes **144** for the preparation of β-hydroxysulfides **247**.

into intermediate **254** *via* HAT from formic acid. Intermediate **254** is subsequently reduced by **253**, generating oxygen-centered radical **257**. A final hydrogen atom abstraction from the formate anion leads to the formation of the final product **247**, along with the regeneration of radical anion species **251**.

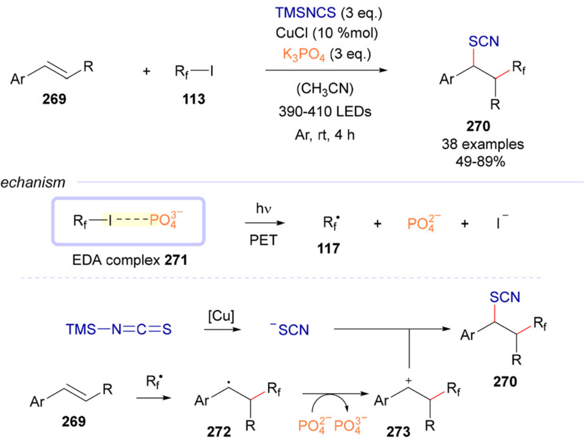
One of the most recent works in the field of photochemical $C(sp^3)$–S bond formation with hydrogen-bonding EDA complexes has been developed by Li and Wen (Scheme 37).[66] In this study, a regioselective (Markovnikov or *anti*-Markovnikov) 1,2-difunctionalization of alkenes derived from lactams **256** produces in a selective manner thioethers **257**, **258** or **259**. Interestingly, the choice of the solvent for the reaction is critical to dictate the regiochemistry of this transformation, where charge transfer (CT) can be favoured over energy charge transfer (E_n-CT) depending on the solvent. Initially, exposure to the EDA complex **260** to visible light triggers a rapid electron transfer within the THF/DBE solvent system, resulting in the generation of radical anion **261** and radical cation **262**. The Markovnikov hydrothiolation product **257** is efficiently obtained through radical cross-coupling of these intermediates in the THF/DBE mixture. In contrast, the formation of the *anti*-Markovnikov hydrothiolation product **258** appears to be linked to a slower E_n-CT process that occurs when the H-bonding EDA complex **260** is exposed to light in an ether-based solvent. Additionally, sulfur radical **264** and radical anion **261** are produced under visible light irradiation when the reaction is conducted in THF with K_2HPO_4 acting as a base, being the formation of EDA complex **263** critical. The carbon-centered radical **268** emerges from the oxidation of carbanion intermediate **267** by sulfur radical **264**, while intermediate **265** itself is generated through the *anti*-Markovnikov cross-coupling of **261** and **264**. Subsequently, the carbon-centered radical **266** reacts with O_2, forming the peroxy radical intermediate **267**. The desired *anti*-Markovnikov hydroxysulfenylation product



Scheme 37 Light-driven excitation of hydrogen-bonding EDA-complexes enables the preparation of compounds **257**, **258** and **259**.

259 is then produced *via* its interaction with compound **104**, releasing sulfoxide radical **268**.

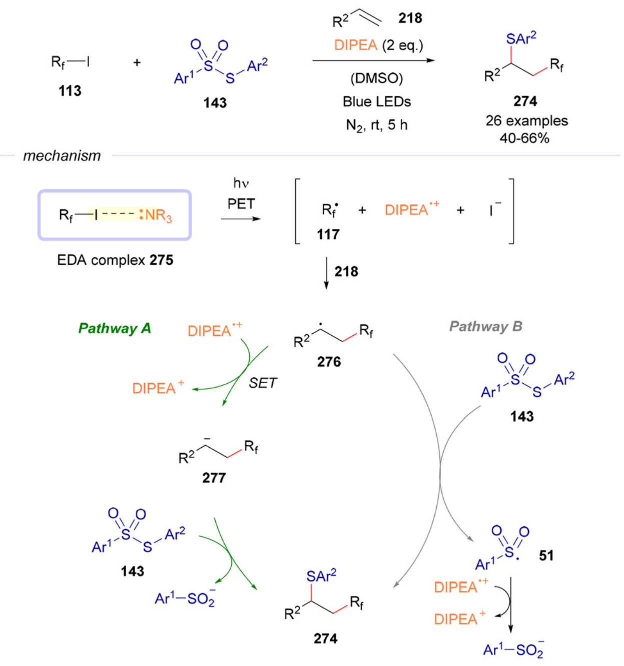
2.3.2. Activation of the electron acceptor with a sacrificial donor. In 2021, Guo and co-workers reported a photochemical fluoroalkylthiocyanation of olefins **269** (Scheme 38).[67] This multicomponent reaction proceeds by mixing alkenes **269**, per-



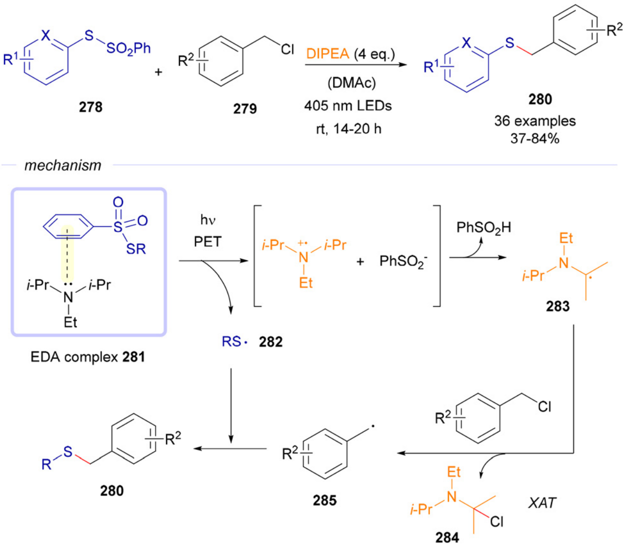
Scheme 38 Fluoroalkylthiocyanation of alkenes **269** based on the employment of K_3PO_4 as the sacrificial donor.

fluoroalkyl iodides **113**, TMSNCS, and potassium phosphate as a base, with a copper catalyst required for the transformation. In solution, an EDA complex **271** forms between the sacrificial donor phosphate anion and the electrophilic perfluoroalkyl iodide **113**, generating the perfluoroalkyl radical **117** along with a phosphite anion. The perfluoroalkyl radical **117** then adds to olefin **269**, forming a carbon-centered radical **272**, which is subsequently oxidized by the phosphite anion to yield the carbocationic intermediate **273**. Meanwhile, TMSNCS interacts with the copper catalyst, leading to the *in situ* formation of a thiocyanate anion. This anion then recombines with **273**, affording the final products **270**.

In 2024, Liu's group developed a multicomponent, visible-light-driven perfluoroalkylation–thiolation reaction of alkenes, utilizing sacrificial donors to form electron donor–acceptor complexes (Scheme 39).[68] In this approach, thiosulfones **143** serve as the thiolating agent, while DIPEA acts as a sacrificial donor within the EDA complex **275**, in combination with perfluoroalkyl iodides **113**. Photochemical fragmentation of the aggregate generates the perfluoroalkyl radical **117** and the DIPEA radical cation. Radical addition of **117** to olefin **218** produces an alkyl-centered radical intermediate **276**, which can undergo two main pathways to yield the final products **274**. Pathway A contemplates a reduction of intermediate **276** by the DIPEA radical cation, affording the carbanionic species **277**. At this point a nucleophilic substitution on the thiosulfone **143** takes place, forming compound **274** and a sulfinate anion. On the other hand, pathway B is based on a radical substitution reaction of **276** on **143**, generating this way the thioether **274**, along with a sulfonyl radical **51**. The latter radical intermediate is transformed into the corresponding sulfinate anion through reduction from the DIPEA radical cation.



Scheme 39 1,2-Perfluoroalkylation/thiolation reactions of alkenes **218** for the preparation of thioethers **274**.



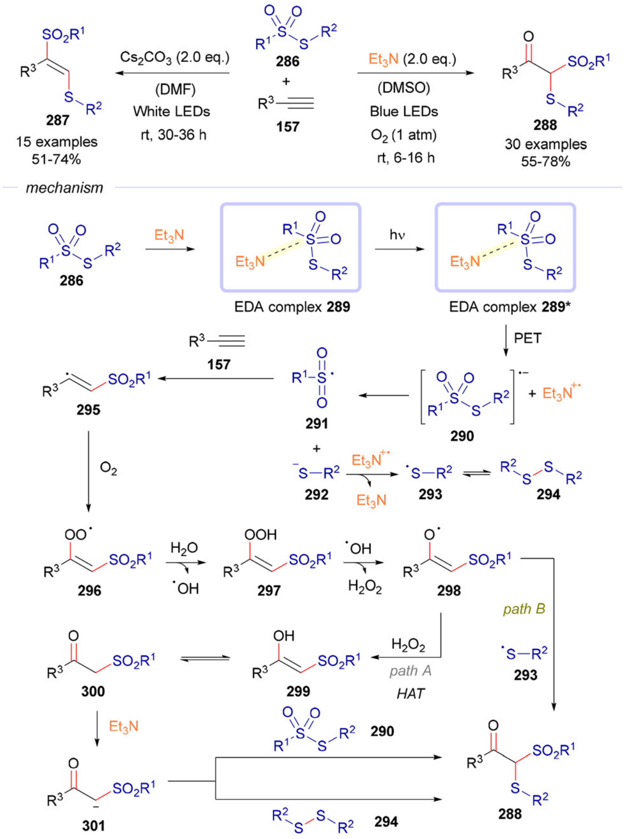
Scheme 40 Thioetherification reactions of benzyl chlorides **279** to form the benzyl thioethers **280**.

A different transformation involving EDA complexes for $C(sp^3)$–S bond formation was reported by Wu and Wang (Scheme 40).[69] In this work, thiosulfones **278** again serve as the thiolating agent, this time in the thiolation of benzyl chlorides **279**.

The cross-coupling reaction proceeds *via* the formation of an EDA complex **281**, where DIPEA acts as the electron donor, and thiosulfone **278** serves as the electron acceptor. Upon light-driven fragmentation, the complex breaks into a sulfur-centered radical **282**, a DIPEA radical cation, and a sulfinate anion. The sulfinate anion then deprotonates the DIPEA radical cation, producing a carbon-centered radical **283**. This radical undergoes a halogen atom transfer (XAT) reaction with benzyl chloride **279**, abstracting a chlorine atom and forming the benzyl radical **285**, along with stoichiometric amounts of compound **284**. Finally, radical recombination between **282** and **285** yields the benzyl thioethers **280**.

The final study covered in this section was recently reported by the group of Patel (Scheme 41).[70] In this study, functionalization reactions of alkynes **157** were explored with thiosulfonates **286**.

Depending on the reaction conditions, an oxidative functionalization to form compounds **288** or vicinal difunctionalization to create products **287** can be achieved. For the mechanistic discussion, only the $C(sp^3)$–S bond forming reaction will be contemplated. In this case, the thiosulfonate **286** forms an EDA complex **289** with Et_3N. Upon exposure to visible light, this complex transitions into an excited state (**289***), leading to a single electron transfer from Et_3N to **286**. This process generates a radical anion **290**, which subsequently undergoes S–S bond cleavage, producing a sulfonyl



Scheme 41 Photochemical regioselective vicinal and oxidative geminal functionalization of alkynes **157**.

radical **291** and a thiolate anion **292**. The thiolate anion **292** is then oxidized by the triethylamine radical cation, yielding a thiyl radical **293**, which dimerizes to form diphenyl disulfide **294**. Simultaneously, the sulfonyl radical **291** reacts with the acetylene **157**, forming a vinyl sulfonyl radical **295**. This radical is intercepted by molecular oxygen to produce a peroxo intermediate **296**, which subsequently interacts with moisture (H_2O) in the reaction medium, forming a hydroxoperoxyl intermediate **297** and releasing hydroxyl radicals. The intermediate **297** then reacts with the hydroxyl radical, generating intermediate **298** and releasing H_2O_2. Following this, a hydrogen atom transfer from H_2O_2 to **298** results in the formation of an enol intermediate **299**, which undergoes tautomerization to yield the β-keto sulfone **300**. Finally, in the presence of Et_3N, the β-keto sulfone reacts either with thiosulfonate **290** or with the *in situ* generated diphenyl disulfide **294**, leading to the formation of the trifunctionalized product **287** (path a). Alternatively, product **287** can also be formed *via* radical–radical cross-coupling between intermediate **298** and the thiyl radical **293** (path b).

In summary, recent years have seen significant advancements in C(sp^3)–S bond-forming reactions *via* photochemical excitation of EDA complexes. Several research groups have focused on developing methodologies that leverage various nucleophilic donors (primarily thiols, thioethers, and thiosulfonates) in combination with electron acceptors such as Katriztky salts, organic halides, redox-active esters, and dihydropyridines. Additionally, strategies employing sacrificial donors, particularly amines and inorganic bases, have emerged as effective approaches for facilitating these transformations.

3. Conclusions

The photochemical activation of electron donor–acceptor (EDA) complexes has emerged as a highly efficient and sustainable strategy for C–S bond formation. This review has demonstrated how EDA complexes facilitate single-electron transfer (SET) processes under mild conditions, enabling the selective construction of C–S bonds without the need for harsh reagents, expensive catalysts, or metal-based systems. The discussed methodologies highlight key advantages of EDA complex photochemistry, including improved functional group tolerance, operational simplicity, and alignment with green chemistry principles. These features make it an attractive alternative to traditional approaches, such as nucleophilic substitution and metal-catalyzed cross-coupling. Continued research in this area will likely uncover new methodologies and applications, further solidifying the role of EDA complex photochemistry as a transformative tool for sustainable C–S bond formation.

Author contributions

H. F. P and I. T. contributed equally to the literature review, analysis, and drafting of the figures and schemes of the manuscript. M. P. conceptualized and supervised the overall study and wrote the manuscript. All authors discussed the content, contributed to the writing, and reviewed the final version of the manuscript.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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