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Recent advances in the synthesis of benzo[*b*]thiophene fused polycyclic derivatives: Strategies and reactions

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ABSTRACT

Benzo[*b*]thiophene fused compounds with a unique active heterocyclic skeleton have wide applications in the fields of medicinal chemistry, organic synthesis, and organic functional materials, which resulted in rapid development of many efficient methods for the construction of benzo[*b*]thiophene-fused heterocycles in recent years. Among these methods, the domino reaction of benzo[*b*]thiophene derivatives is a practical and powerful synthetic route to access benzo[*b*]thiophene-fused heterocycles by virtue of the particularity of sulfur atom. This review summarizes the latest developments in the construction of benzo[*b*]thiophene-fused heterocycles by ring formation at the C2-C3-position of benzo[*b*]thiophene derivatives in the past decade. Additionally, this review is divided into four parts according to the four kinds of benzo[*b*]thiophene derivatives used, including thioaurone, thioisatin, substituted benzo[*b*]thiophene, and azadiene.

1. Introduction

Benzo[*b*]thiophene with a unique hybrid skeleton is an important core component for the construction of benzo[*b*]thiophene fused heterocycles, which have been widely used in the synthesis of organic compounds, multifunctional materials and drug molecules. Benzo[*b*]thiophene fused compounds not only have unique chemical properties and biological activities, but also have excellent pharmacological properties and metabolic stability. They are widely present in organic functional materials [1–8] and drug molecules, such as NU7441 [9] and Y-931 (Fig. 1) [10]. The synthesis of multifunctional benzo[*b*]thiophene fused heterocycles plays an important role in the fields of organic synthesis methodology and functional material chemistry and have attracted extensive attention of scientists in recent years [11–14].

In recent years, chemical researchers have made great progresses in the efficient construction of benzo[*b*]thiophene fused heterocycles, and a series of versatile synthetic methods have been exploited on the basis of the reactivities of thioaurone, thioisatin, benzo[*b*]thiophene, and azadiene.

Scheme 1 shows four classic pathways for the synthesis of benzo[*b*]thiophene fused cyclic compounds. In the first one, thioaurone reacts with a 1,3- or 1,4-dipolar zwitterion, which is followed by proton transfer, and the final addition/elimination process gives the product (Scheme 1A). In the second one, the C-S bond cleavage of thioisatin by nucleophilic attack of an amine leads to a sulfur anion intermediate, which undergoes a nucleophilic S-alkylation with α-haloketones, annulation, dehydration, and intramolecular nucleophilic addition, in succession, to give benzo[*b*]thiophene fused heterocycles (Scheme 1B). In the third one, the addition of a five-membered metallacycle to the C2 position of benzo[*b*]thiophene through C–H activation results in C2-metallation, which is followed by an elimination process to generate a biaryl compound. Afterwards, it may undergo a cyclization process to give the corresponding product, or continue a further reaction at the β-position of benzo[*b*]thiophene skeleton under the catalysis of metal catalyst to afford the desired product through a reductive elimination step (Scheme 1C). In the last one, Morita–Baylis–Hillman (MBH) carbonate expels a CO_2 and *tert*–butoxy anion under the action of a Lewis base and then undergoes a γ-addition reaction with azadiene to generate a remote zwitterion intermediate with two resonance structures. Finally, an intramolecular substitution reaction with the removal of the catalyst 4-dimethylaminopyridine (DMAP) produces the final product (Scheme 1D).

The following sections will summarize the advances on the construction of benzo[*b*]thiophene fused polycyclic derivatives in the

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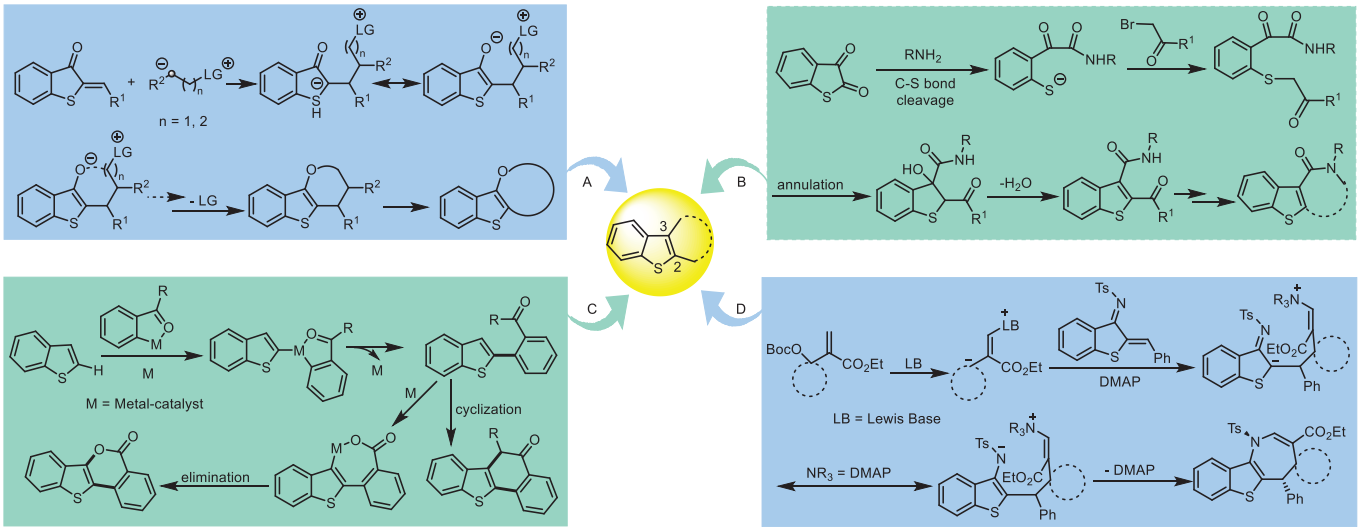


Scheme 1. Classic pathways for the synthesis of benzo[*b*]thiophene fused cyclic compounds.

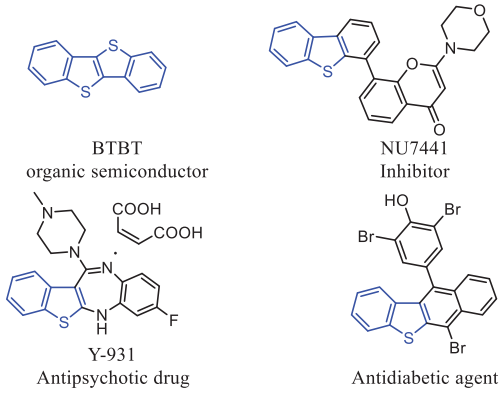


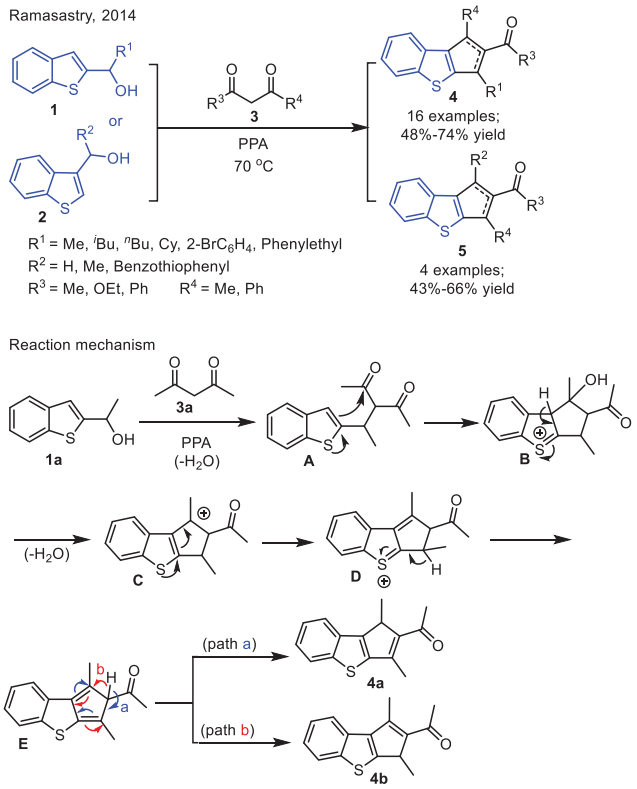
Fig. 1. Pharmaceuticals and bioactive molecules containing benzo[*b*]thiophene scaffolds.

last decade, including the contributions of our group and others, with a particular attention paid to the reaction mechanism (Scheme 1). The applications of these benzo[*b*]thiophenes are beyond the scope of this review.

2. Synthesis of benzo[*b*]thiophene fused polycyclic derivatives from substituted benzo[*b*]thiophene

2.1. The [3+2] annulation reaction of substituted benzo[b]*thiophenes*

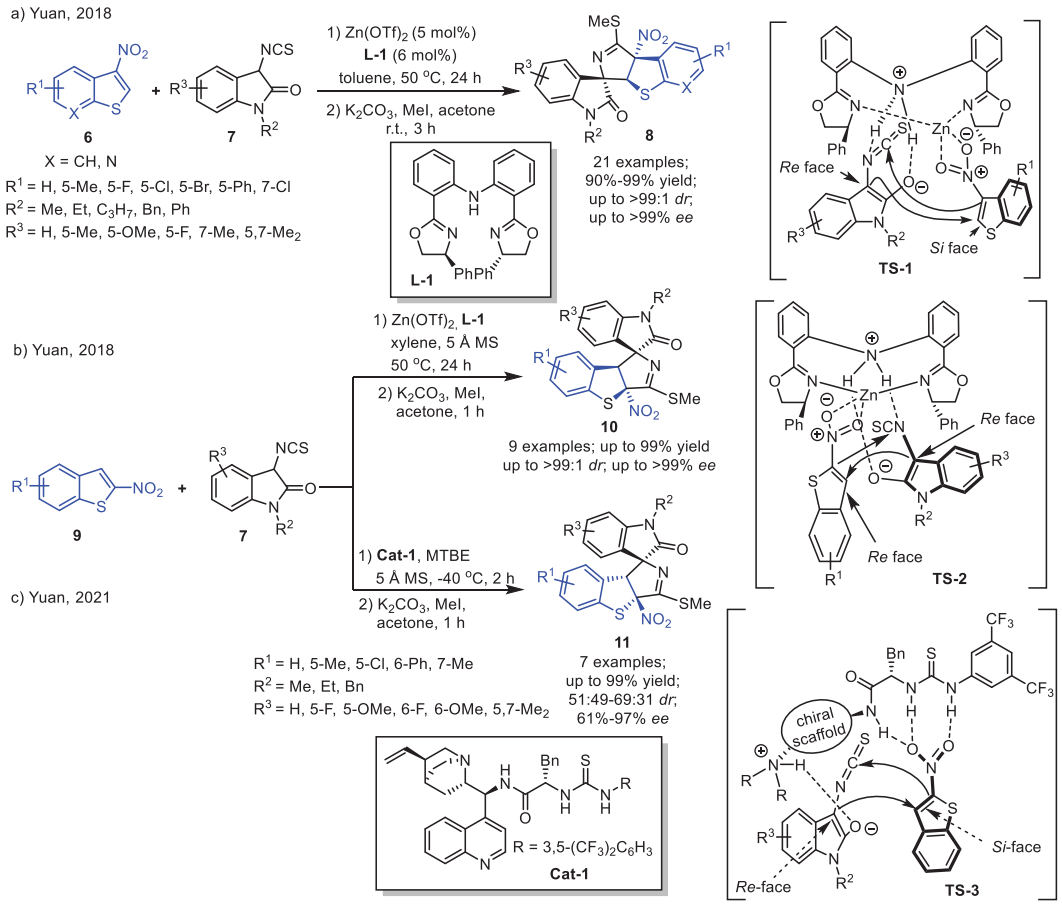
Benzo[*b*]thiophenes have various practical functions and are present in many pharmaceutical drugs and organic semiconductor materials [15–18]. In recent years, a number of methodologies have been developed on the basis of [3+2] annulation reaction of benzo[*b*]thiophenes for the synthesis of various benzo[*b*]thiophene fused polycyclic derivatives. In 2014, Ramasastry *et al.* designed a solvent-free domino reaction to form cyclopentannulated benzo[*b*]thiophenes (**4** and **5**) from benzothienyl carbinols (**1** and **2**) and 1,3-dicarbonyls **3** under the condition of polyphosphoric acid (PPA) (Scheme 2) [19]. Mechanistic investigation suggested that **1a** initially reacted with **3a** to produce intermediate **A**, and a subsequent intramolecular cyclization formed intermediate **B**, which could be converted to intermediate **C** through elimination of H_2O. Then, species **D**, another resonance structure



Scheme 2. Synthesis of cyclopentannulated benzo[*b*]thiophenes by solvent-free domino reaction.

of **C**, evolved to intermediate **E** by loss of a proton. Finally, **E** could be converted to either **4a** *via* path a or **4b** *via* path b.

In 2018, Yuan *et al.* developed a highly efficient dearomative reaction for the synthesis of benzo[*b*]thiophene fused polycyclic derivatives **8** from 3-nitrobenzo[*b*]thiophenes **6** and 3-isothiocyanato oxindoles **7** (Scheme 3a) [20]. The use of $Zn(OTf)_2$ and chiral ligand **L-1** as catalyst gave a series of benzo[*b*]thiophene fused polycyclic derivatives **8** in excellent yields with high enantioselectivities and diastereoselectivities. However, no product was observed for the reaction with 2-methyl-3-nitrobenzo[*b*]thiophene



Scheme 3. The dearomative reaction of benzo[*b*]thiophenes.

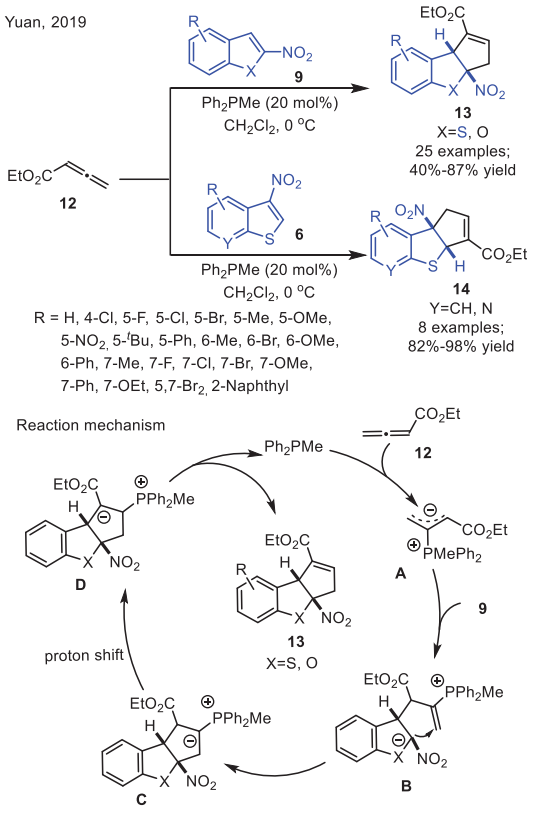
due to a steric hindrance. Gram scale experiments gave the desired product in 99% yield, demonstrating the practicality of this strategy.

In the same year, Yuan *et al.* also reported the reaction between 2-nitrobenzo[*b*]thiophenes **9** and 3-isothiocyanato oxindoles **7** with the same catalyst as that in Scheme 3a in a different solvent (Scheme 3b) [21]. Broad substrate scope was verified by the observation that substrates with various substituents at the N position or various groups on the aromatic rings were well tolerated to afford the cycloadducts **10** in excellent yields with high *dr* and *ee* (up to >99:1 *dr* and >99% *ee*). They proposed a possible transition state (**TS-2**) to understand the stereochemistry during the formation of cycloadducts **10**. Dearomative annulation of heteroarenes has become an effective way for the construction of polycyclic heterocycles [22]. In the subsequent work, Yuan and co-workers developed a **Cat-1**-catalyzed dearomative reaction of 2-nitrobenzo[*b*]thiophenes **9** and 3-isothiocyanato oxindoles **7** in methyl *tert*–butyl ether (MTBE) in 2021 (Scheme 3c) [23]. Followed by treating with K_2CO_3 and CH_3I in acetone, the reaction successfully furnished a wide range of polycyclic heterocyclic products **11** with consistent (*R, R, S*) configurations. Experimental results demonstrated the efficiency of this reaction and the potential for building benzo[*b*]thiophene fused polycyclic derivatives.

In 2019, Yuan's group reported a Ph_2PMe-catalyzed [3 + 2] cyclization of 2-nitrobenzo[*b*]thiophenes **9** or 3-nitrobenzo[*b*]thiophenes **6** with allenoates **12** (Scheme 4) [24]. A wide range of structurally diverse cyclopenta[*b*]benzothiophenes (**13** and **14**) were obtained in good to excellent yields. A plausible reaction mechanism was shown in Scheme 4. Catalytic Ph_2PMe was first added to the sp-carbon atom of 2,3-butadienoate **12** to form intermediate **A**, which gave intermediate **B** through a conjugate addition with **9**. Intermediate **C** was formed by an intramolecular annulation process and then was converted into intermediate **D** through an intramolecular proton shift process. Finally, intermediate **D** released Ph_2PMe and afforded product **13**.

In 2020, Wang *et al.* investigated a new approach for the synthesis of fused tricyclic benzo[*b*]thiophene compounds (**16** and **17**) from nitrobenzo[*b*]thiophenes (**6** and **9**) and nonstabilized azomethine ylides **15′** (Scheme 5a) [25]. Optimizations of experimental variables showed that CH_2Cl_2 solution of trifluoroacetic acid (TFA) at room temperature was the best choice. This method efficiently gave the corresponding products in good to excellent yields. In 2021, Wang's group found the ability of **Cat-2** to catalyze the reaction of 2-nitrobenzo[*b*]thiophenes **9** and azomethine ylides **18** (Scheme 5b) [26]. The transformation proceeded through an asymmetric Michael/Mannich cascade reaction and successfully furnished the desired dihydrobenzo[*b*]thiophene polycyclic products **19**. They proposed plausible catalytic cycles of the reaction in Scheme 5b. The initial reaction of **Cat-2** with **18** through a deprotonation process produced intermediate **A**, which subsequently underwent a Michael addition with **9**, *via* transition state **B**, to form Michael adduct **C**. Intermediate **E** was generated through an intramolecular Mannich reaction, *via* transition state **D**, and eventually evolved to the desired product **19**.

In 2019, Yuan's group performed the reaction of ethyl 4-mercapto-2-butanoate **20** with **6** using different catalysts and temperatures (Scheme 6) [27]. With the use of **Cat-3** or **Cat-4** as the catalyst for the case of X = S or X = N-R in **6**, respectively, a series of chiral benzo[*b*]thiophene heterocyclic molecules **21** or tetrahydrothiopheneindoline derivatives **22** were obtained in good to ex-



Scheme 4. Ph_2PMe-catalyzed reaction of nitrobenzo[*b*]thiophenes and allenoates.

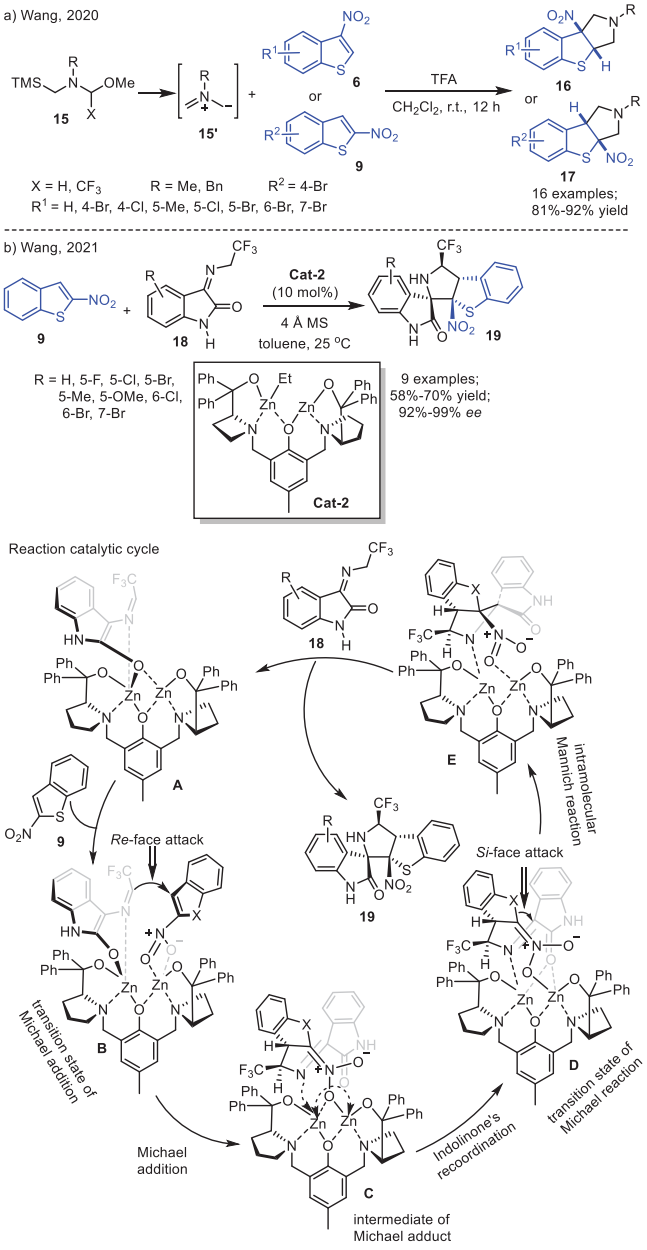
cellent yields, providing a creative method to access these two types of compounds.

In 2021, John's group discovered a metal-free, one-pot reaction for the synthesis of benzo[*b*]thiophene-fused heteroacenes (**24**, **26** and **28**) (Scheme 7) [28]. 3-Nitrobenzo[*b*]thiophenes **6** were employed to react with various phenols (**23**, **25** and **27**) in the presence of KOH and EtOH at 80 °C. The reaction mechanism suggested that phenol **27** first reacted with **6** to form intermediate **A**, which was followed by an intramolecular cyclization to give intermediate **B**. Finally, intermediate **B** was converted to **28** by eliminating HNO and H_2O.

2.2. The [4 + 2] annulation reaction of benzo[b]thiophenes

The [4 + 2] cycloaddition reaction has been proved to be one of the most effective methods to obtain polycyclic heterocyclic skeletons and also a powerful way to construct multifunctional benzo[*b*]thiophene-fused heterocycles. In 2014, Mohanakrishnan *et al.* developed an efficient method for the preparation of benzo[*b*]thiophene-annulated heterocycles **31** in CH_2Cl_2 *via* a Lewis acid/Bronsted acid mediated cyclization of substituted benzo[*b*]thiophenes **29** and 2,5-dimethoxytetrahydrofuran **30** (Scheme 8) [29]. This reaction used **30** as the four-carbon synthon and successfully gave the target products **31** in good to excellent yields.

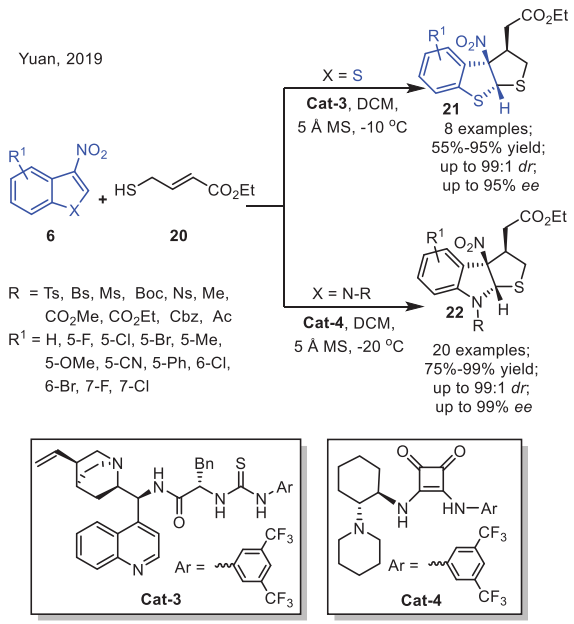
In the same year, Chen's group developed an asymmetric dearomatic Diels-Alder reaction of maleimides **32** and benzo[*b*]thiophene derivatives (**33**, **35** and **37**) under the catalysis of cinchona-based primary amine **Cat-5**. Benzo[*b*]thiophene-fused derivatives with different configurations (**34**, **36** and **38**) were obtained in excellent yields under different conditions (Scheme 9) [30].



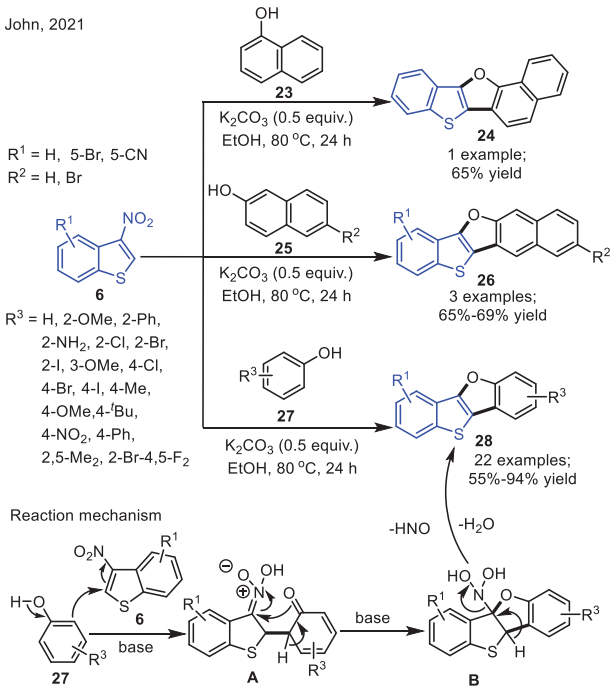
Scheme 5. The [3 + 2] reaction of nitrobenzo[*b*]thiophenes and azomethine ylides.

In 2019, Noland and co-workers developed a Diels-Alder reaction between maleimides **32** and 2-(1′-cycloalkenyl) benzo[*b*]thiophene **39** to produce dibenzo[*b,d*]thiophene derivatives (**40** and **41**) in excellent yield (Scheme 10) [31]. The cycloalkenyl group at C2 position of benzo[*b*]thiophene could be five-, six-, seven-, eight- and twelve-membered rings, broadening the substrate range of the reaction. The use of *N*-phenylmaleimides generated normal Diels-Alder adducts **40**, while the use of *N*-methylmaleimide generated rearranged Diels-Alder adducts **41.**

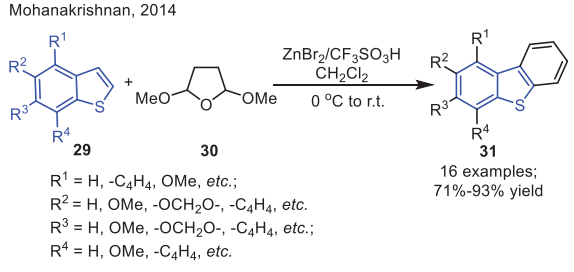
In 2019, Yuan *et al.* developed an aza-Michael/Michael addition cascade reaction between 2-nitrobenzo[*b*]thiophenes **9** and 2-aminochalcones **42** in the presence of CH_2Cl_2 at room temperature, with the use of chiral bifunctional squaramide **Cat-4** as the catalyst (Scheme 11) [32]. The reaction enabled the synthesis of chiral benzo[*b*]thiophene fused heterocyclic compounds **43** under mild reaction conditions. It was worth noting that higher yields were obtained using 2-nitrobenzofuran derivatives (X = O) as



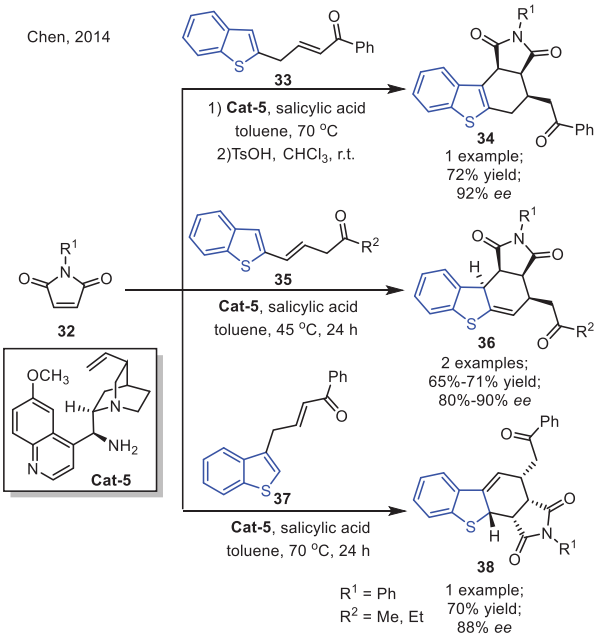
Scheme 6. Organocatalytic asymmetric dearomatization reaction of 3-nitroindoles and 3-nitrobenzo[*b*]thiophenes with ethyl 4-mercapto-2-butenoate respectively.



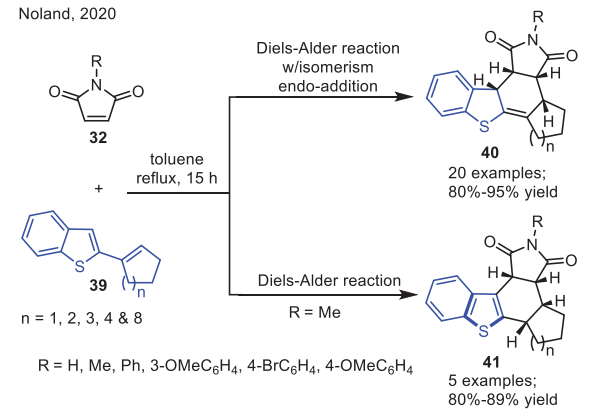
Scheme 7. The metal-free one-pot reaction of 3-nitrobenzo[*b*]thiophenes and various phenols.



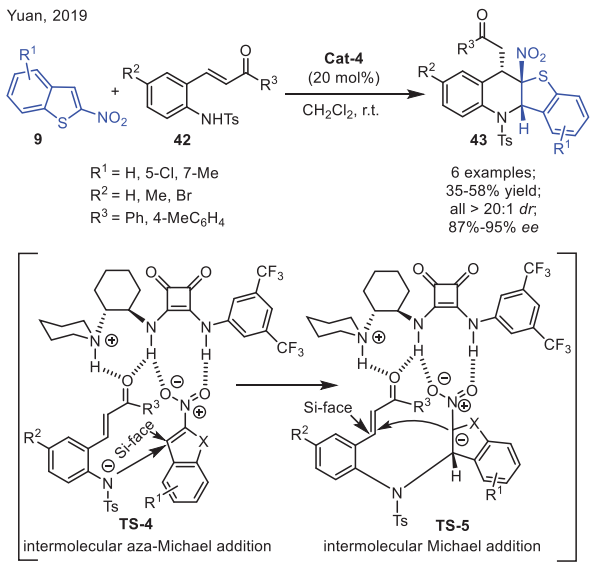
Scheme 8. Synthesis of benzo[*b*]thiophene-annulated heterocycles from substituted benzo[*b*]thiophenes and 2,5-dimethoxytetrahydrofuran.



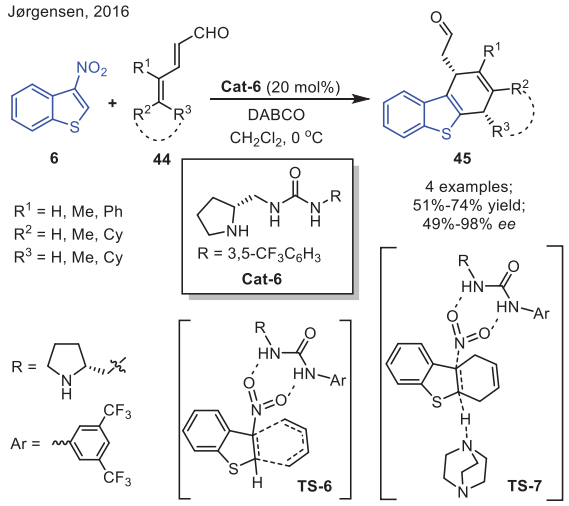
Scheme 9. Synthesis of fused benzo[*b*]thiophene derivatives *via* Diels-Alder reaction.



Scheme 10. Synthesis of dibenzo[*b,d*]thiophene derivatives *via* Diels-Alder reaction.



Scheme 11. Synthesis of heterocyclic fused compounds by aza-Michael/Michael addition cascade reaction.



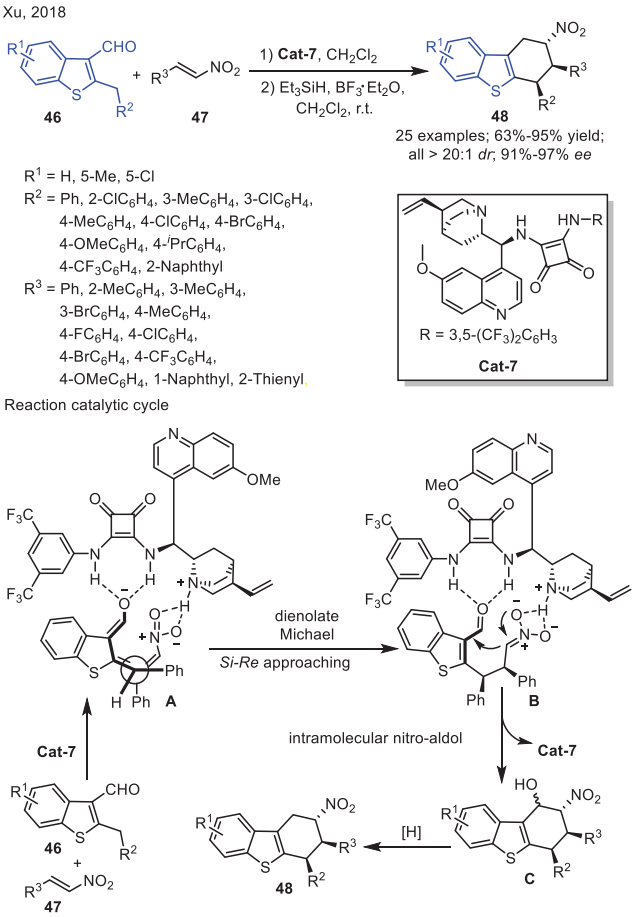
Scheme 12. Synthesis of benzo[*b*]thiophene-fused derivatives from benzo[*b*]thiophene derivatives and 2, 4-dienals derivatives.

substrates than using 2-nitrobenzo[*b*]thiophene derivatives (X = S). The authors proposed two transition state models (**TS-4** and **TS-5**) involving intramolecular aza-Michael addition and intramolecular Michael addition, respectively.

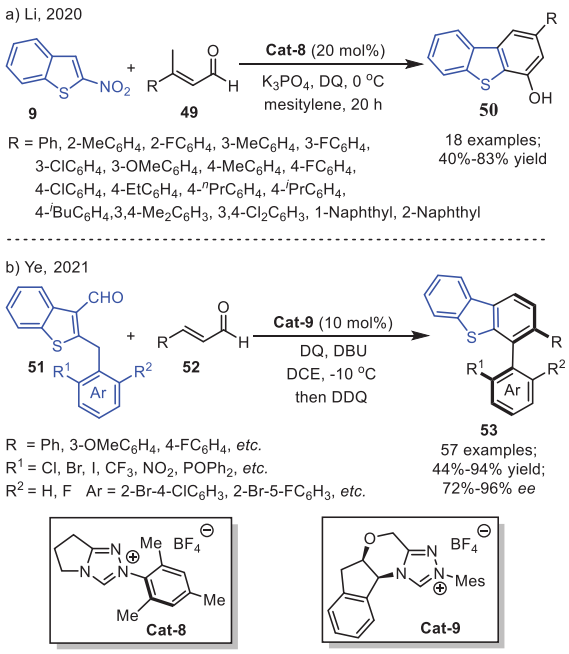
In 2016, the first enantioselective [4 + 2] cycloaddition of 3-nitrobenzo[*b*]thiophenes **6** with 2,4-dienals **44** was established by Jørgensen's group (Scheme 12) [33]. The use of **Cat-6** as the catalyst and 1,4-diazobicyclo[2.2.2]octane (DABCO) as the additive delivered chiral benzo[*b*]thiophene fused cycloadducts **45** in moderate to good yields with moderate to excellent enantioselectivities. Mechanistic studies suggested that the reaction proceeded through asynchronous/stepwise addition and elimination processes, and the transition states (**TS-6** and **TS-7**) of the addition and elimination steps were presented in Scheme 12.

In 2018, Xu's group reported **Cat-7** catalyzed cyclization of benzo[*b*]thiophene-3-carbaldehydes **46** and nitroolefins **47** to afford tetrahydrodibenzo[*b*]thiophene derivatives **48** in good to excellent yields with high enantioselectivities (Scheme 13) [34]. From the viewpoint of reaction mechanism, **46** first reacted with nitroolefins **47** to form intermediate **A** under the catalysis of **Cat-7**, which was followed by an asymmetric Michael addition process to form intermediate **B**. Subsequently, intermediate **B** was converted to **C** through an intramolecular nitro-aldol reaction with release of **Cat-7**. Finally, the desired product **48** was produced by a dehydration/reduction process from **47**.

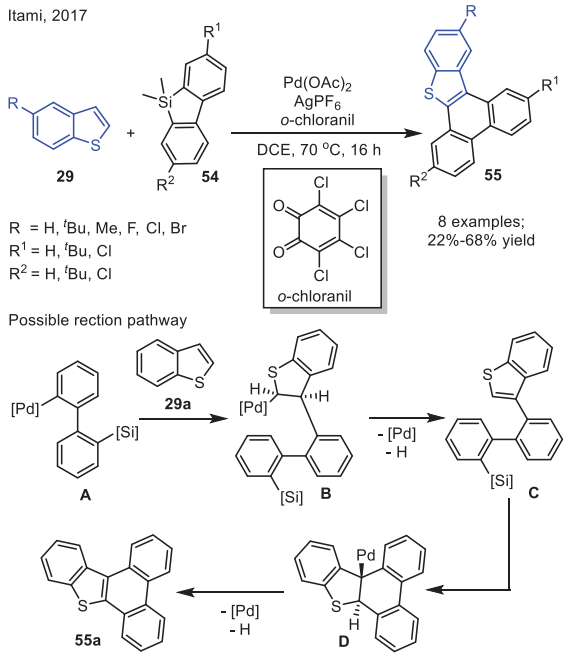
As powerful tools in organic synthesis, *N*-heterocyclic carbene (NHC) organocatalysts have attracted extensive attention in recent years [35–38]. In 2020, Li's group reported an oxidative cascade reaction between 2-nitrobenzo[*b*]thiophene **9** and β-substituted crotonaldehydes **49** in the presence of the NHC catalyst **Cat-8** and 4,4′-diphenoquinone (DQ). This strategy rapidly accessed a series of 4-hydroxydibenzo[*b*]thiophenes **50** in moderate to good yields (Scheme 14a) [39]. In 2021, Ye's team put forward a methodology for the enantioselective synthesis of a series of chiral benzo[*b*]thiophene-fused biaryls **53**, by using 2-benzylbenzo[*b*]thiophene-3-carbaldehydes **51** and β-aryl enals **52** as substrates, **Cat-9** as the NHC catalyst, DQ as oxidant, 1,8-diazabicylo-[5.4.0]undec–7-ene (DBU) as base, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as the second oxidant (Scheme 14b) [40]. This methodology benefited from a broad substrate scope and unique chemoselectivity. Gram-scale experiments furnished the desired products in high yields (up to 92% yield) and high enantioselectivities (up to 98% *ee*), which disclosed the prac-



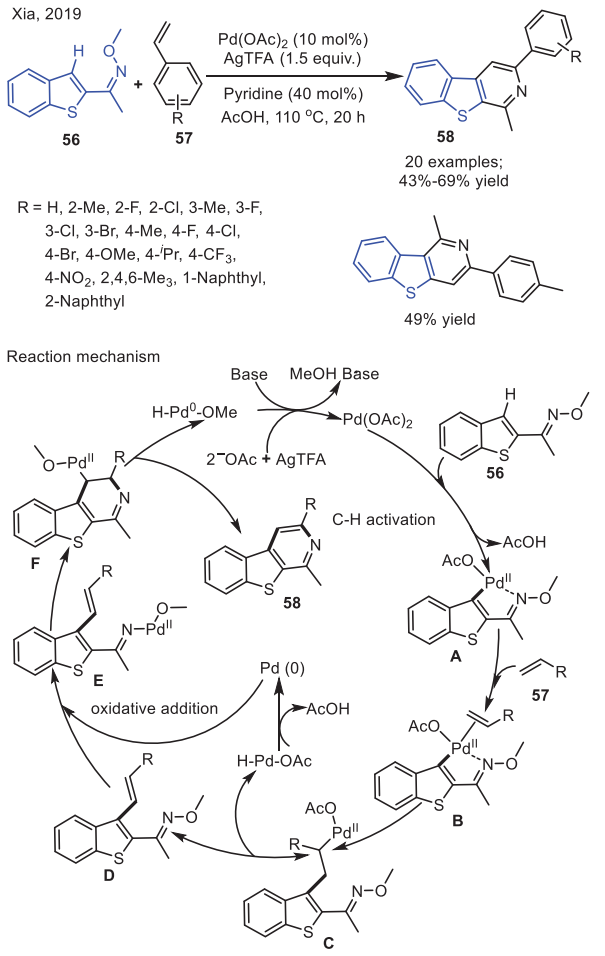
Scheme 13. Synthesis of tetrahydrodibenzo[*b*]thiophene derivatives from benzo[*b*]thiophene-3-carbaldehydes and nitroolefins.



Scheme 14. Synthesis of benzo[*b*]thiophene-fused derivatives *via* NHC catalysis.



Scheme 15. Pd-catalyzed cyclization of benzo[*b*]thiophenes with 9,9-dimethyldibenzosiloles.



Scheme 16. Pd-catalyzed synthesis of benzothienopyridines.

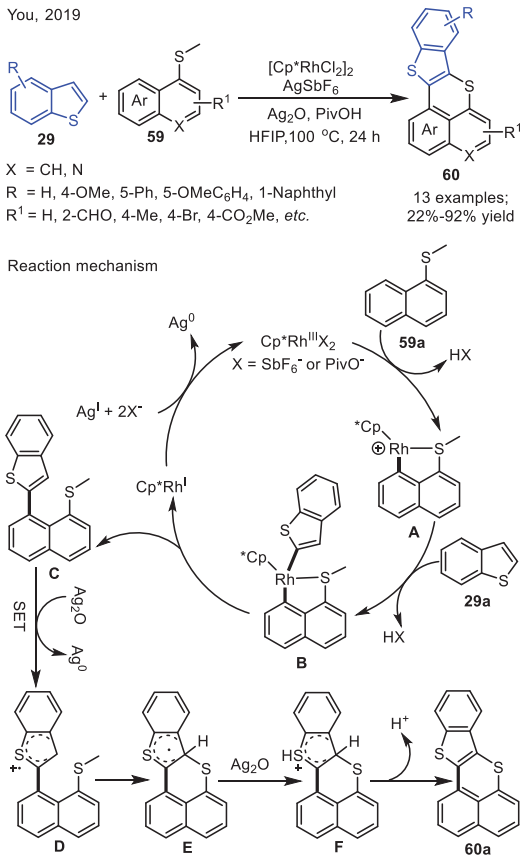
ticality of the strategy and provided an efficient route for the synthesis of axially chiral benzo[*b*]thiophene-fused biaryls.

In recent years, transition-metal-catalyzed cyclization reaction has emerged as a highly efficient strategy for building benzo[*b*]thiophene fused heteroaromatic compounds [41–44]. In 2017, Itami's group developed an efficient π-extension reaction of benzo[*b*]thiophenes **29** with 9,9-dimethyldibenzosiloles **54** to produce benzo[*b*]thiophene-fused heteroarenes **55** (Scheme 15) [45]. Under the palladium/*o*-chloranil catalytic system, the π-extended fused heteroarenes **55** could be obtained in a single step. A possible reaction pathway was proposed by the authors. The reaction was initiated by the formation of intermediate **A**, which reacted with benzo[*b*]thiophene **29a** to form β-biphenyl-α-palladated adduct **B**. Subsequently, **B** underwent a β-H elimination/demetallation processes to give intermediate **C**, which was further converted to intermediate **D** through the sequential transmetalation and carbopalladation processes. Finally, product **55a** was obtained by a β-H elimination/demetallation process from intermediate **D**.

In 2019, Xia and co-workers reported the palladium-catalyzed reaction of *O*-methylketoxime **56** with styrenes **57**. Under the catalysis of $Pd(OAc)_2$ in AcOH at 110 °C, a series of benzothienopyridines **58** were obtained in moderate yields (Scheme 16) [46]. The reaction mechanism showed that intermediate **A** was formed by coordination of **56** to $Pd(OAc)_2$ and then was converted to intermediate **B**. Ring-open of intermediate **B** led to intermediate **C**, which was further transformed into intermediate **D** with release of AcOH and Pd(0). The oxidative insertion of Pd(0) into the N-O bond resulted in intermediate **E**, which evolved to intermediate **F** by the C-N bond formation and N-O bond cleavage. Finally, product **58** was obtained after a β-hydride elimination process from intermediate **F**.

In 2019, You's group reported a rhodium-catalyzed annulation between benzo[*b*]thiophenes **29** and 1-(methylthio)naphthalene derivatives **59** in the presence of Ag_2O and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for the construction of polycyclic benzo[*b*]thiophene-fused derivatives **60** (Scheme 17) [47]. In the proposed reaction mechanism, 1-(methylthio)naphthalene **59a** initially coordinated to $Cp^*Rh^{III}X_2$ to form intermediate **A**, which reacted with benzo[*b*]thiophene **29a** to give intermediate **B**. The following reductive elimination process generated intermediate **C**. The released Cp^*Rh^{I} was converted to $Cp^*Rh^{III}X_2$ to re-engage in the catalytic cycles by the oxidation of Ag^{I}. Then, intermediate **C** underwent a single electron transfer (SET) process to give intermediate **D**, after which intermediate **E** was formed *via* an electrophilic cyclization/demethylation process. Finally, **E** was converted to intermediate **F** by the oxidation of Ag_2O, and the expected product **60a** was produced after deprotonation.

In 2021, the same research group disclosed a rhodium-catalyzed cascade annulation of phenacyl phosphoniums **61** and benzo[*b*]thiophenes **29** (Scheme 18) [48]. The use of $[RhCp^*Cl_2]_2$ as catalyst efficiently prepared a series of benzo[*b*]thiophene fused polycyclic compounds **62**. The authors proposed two catalytic cycles (Cycle I and Cycle II) as the candidates of the real reaction pathway. First, **61a** was transformed into **61aa** in the presence of CsOAc, which reacted with $[Rh^{III}Cp^*]$ to yield intermediate **A**. Intermediate **A** reacted with **29a** to form intermediate **B**, and a following β-H elimination process gave intermediate **C**. Then, a C-O bond coupling at **C** afforded intermediate **D**, which underwent β-H elimination to provide intermediate **E** and $[Rh^{I}Cp^*]$. The released $[Rh^{I}Cp^*]$ was converted to $[Rh^{III}Cp^*]$ by the oxidation of Ag_2O to complete the catalytic cycle (Cycle I). Intermediate **E** was further converted to intermediate **F** by C-H activation, followed by a reaction with **29a** to yield intermediate **G**. Then, intermediate **G** underwent β-H elimination to form intermediate **H**, and a C-C bond coupling at **H** gave intermediate **I**. Finally, the β-H elimination of **I**



Scheme 17. Rh-catalyzed annulation reaction of benzo[*b*]thiophenes with naphthalene derivatives.

led to the formation of the target product **62a** and regeneration of [$Rh^{I}Cp^{*}$] (Cycle II).

Iridium-catalyzed annulation reactions of benzo[*b*]thiophene derivatives **29** have been developed for the construction of benzo[*b*]thiophene-fused polyheterocycles. In 2018, Yang and co-workers reported [$IrCp^{*}Cl_2]_2$-catalyzed oxidative cyclization of α-keto carboxylic acids **63** and benzo[*b*]thiophenes **29** (Scheme 19) [49]. A series of benzothieno[3,2-*c*][2]benzopyranones derivatives **64** were successfully obtained with the highest yield of up to 90%. The mechanism was investigated by deuterium-labeling experiments. First, [$IrCp^{*}X_2]_2$ reacted with $AgNTf_2$ to form [Ir^{III}], followed by the coordination of α-keto acid **63a** to produce intermediate **A**. Subsequently, a C-H activation occurring at the C2 position of benzo[*b*]thiophenes **29a** delivered intermediate **B**, and the following reductive elimination process gave intermediate **C** and [Ir^{I}]. Intermediate **C** was converted to intermediate **D** by decarboxylation in the presence of Ag_2O, which was further converted to intermediate **E** by Ag-mediated oxidation. Then, a nucleophilic attack of H_2O transformed intermediate **E** into intermediate **F**, followed by C-H iridation to give intermediate **G**. Reductive elimination of intermediate **G** resulted in the formation of the final product **64a** with release of [Ir^{I}], which was reoxidized to [Ir^{III}] by Ag_2O to finish the catalytic cycle (path a). Alternatively, **63a** could first be converted to benzoic acid **H** through a decarboxylation process, followed by a carbonyl directed C-H activation to afford intermediate **I** (path b). Subsequent reaction of intermediate **I** with **29a** generated intermediate **J**. Reductive elimination from **J** resulted in intermediate **F** and [Ir^{I}], and the processes from [Ir^{I}] to the final product **64a** were the same as those of path a. The authors pointed out that path a may be the main route due to the low efficiency of carboxylic acid **H**, but path b could not be ruled out at this stage.

In 2018, You *et al.* described a one-pot cyclization of benzo[*b*]thiophene derivatives **29** with (hetero)aromatic carboxylic acids **65** or α,β-unsaturated carboxylic acids **67**. Under the catalysis of [$IrCp^{*}Cl_2]_2$, various benzo[*b*]thiophene-fused derivatives (**66** and **68**) were obtained in moderate to good yields (Scheme 20a) [50]. This reaction provided a powerful strategy for the construction of polycyclic benzo[*b*]thiophene-fused compounds. In 2021, Yu *et al.* developed a tandem iridium-catalyzed cross-dehydrogenative coupling reaction of benzo[*b*]thiophene derivatives **29** and ketene dithioacetals **69**, which delivered the target compounds **70** in moderate to good yields (Scheme 20b) [51]. They assumed that the reaction started from a ligand exchange between [$Cp^{*}IrCl_2]_2$, $AgSbF_6$ and $Cu(OPiv)_2$, leading to the formation of [$Cp^{*}Ir^{III}(OPiv)_2$]. The ketene dithioacetal **69a** was then cyclometalated to give intermediate **A**. The reaction of intermediate **A** and benzo[*b*]thiophene **29a** afforded intermediate **B**, and the next reductive elimination process gave species **C** and $Cp^{*}Ir^{II}$. Upon the promotion of Ag_2O, **C** evolved to product **70a** through a radical cyclization reaction. The $Cp^{*}Ir^{II}$ was further converted to [$Cp^{*}Ir^{III}$ $(OPiv)_2$] under the oxidation of Ag_2O and HOPiv.

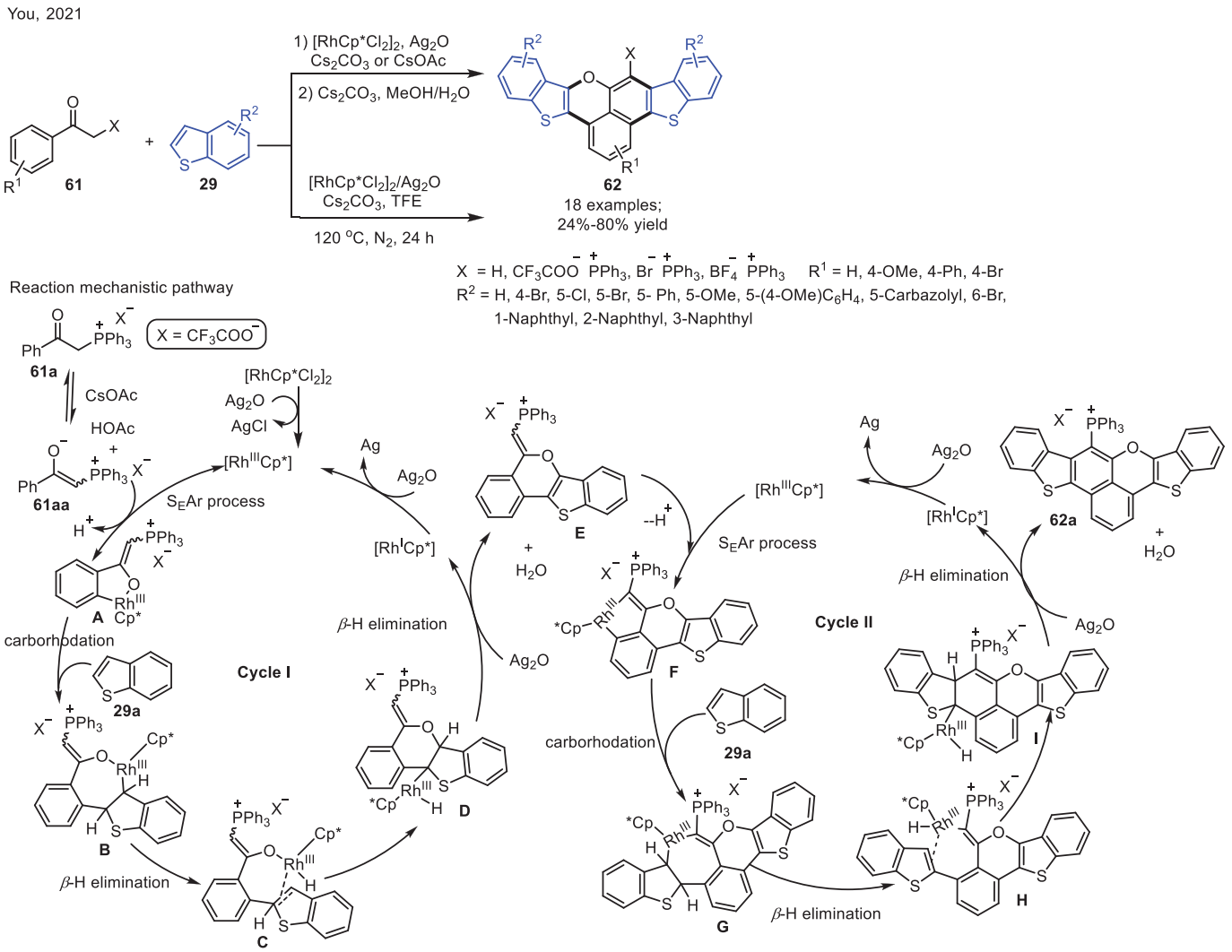
In 2018, Yang's group discovered that the reaction of 3-nitobenzo[*b*]thiophenes **6** and alkylidene malononitriles **71** could produce dibenzothiophen-1-amine derivatives **72** in the presence of triethyamine (TEA) under N_2 atmosphere in CH_3CN at 50 °C, while the yields were not high (Scheme 21a) [52]. In 2020, Yuan and co-workers reported a base-mediated cyclization reaction of nitrobenzo[*b*]thiophenes derivatives (**6** and **9**) with α,α-dicyanoalkenes **73** (Scheme 21b) [53]. Under mild reaction conditions, a series of dibenzoheterocyclic compounds (**74** and **75)** were obtained in good to high yields. This [4 + 2] annulation exhibited a broad substrate scope, and the synthetic utility was well demonstrated by gram-scale experiments.

In 2020, Guo and co-workers reported a chiral phosphine-catalyzed enantioselective [4 + 2] cyclization between 3-nitrobenzo[*b*]thiophenes **6** and allenoates **76**, affording chiral dihydrodibenzo[*b*]thiophenes **77** in good yields with high enantioselectivities. They proposed a mechanism for the reaction. First, allenoates **76** were converted to intermediate **A** under the catalysis of [PR_3'], which further reacted with **6** to produce intermediate **B**. Subsequently, intermediate **B** underwent migration and intramolecular conjugate addition events to regenerate [PR_3'] and form intermediate **D**. The desired product **77** was yielded by eliminating HNO_2 from **D** (Scheme 22) [54].

2.3. Other reactions

Other approaches to access benzo[*b*]thiophene-fused compounds include [4 + 3] cycloaddition and [3 + 3] cycloaddition. In 2013, Li's group developed a [4 + 3] cycloaddition of benzo[*b*]thiophene-3-yl alcohols **78** with 1,3-cyclopentadiene **79** to afford benzo[*b*]thiophene-fused bicyclo[3.2.1]octa-2,6-dienes **80** in moderate to good yields at room temperature (Scheme 23) [55].

In 2018, Deng *et al.* developed an efficient approach for the synthesis of benzo[*b*]thiophene derivatives **83** *via* a [3 + 3] cycloaddition of *N*-Tosyl-3-aminobenzo[*b*]thiophenes **81** and α,β-unsaturated aldehydes **82** under the catalysis of **Cat-11** (Scheme 24) [56]. Coupling reaction has been a powerful and straightforward strategy for the synthesis of various organic compounds [57–60]. In recent years, a large number of heterocyclic benzo[*b*]thiophene fused compounds have been efficiently constructed by means of a coupling reaction. In 2011, Knochel and co-workers reported a synthetic route for the preparation of benzo[4,5]thieno[2,3-*b*]indol derivatives **86** (Scheme 25) [61]. In the first step, 3-bromobenzo[*b*]thiophene **84** was used as substrate to obtain benzo[*b*]thiophen-3-yl zinc(II) chloride, which underwent a Negishi cross-coupling reaction with bromoaniline derivatives **85**



Scheme 18. Rh-catalyzed cascade annulation of phenacyl phosphoniums and benzo[*b*]thiophenes.

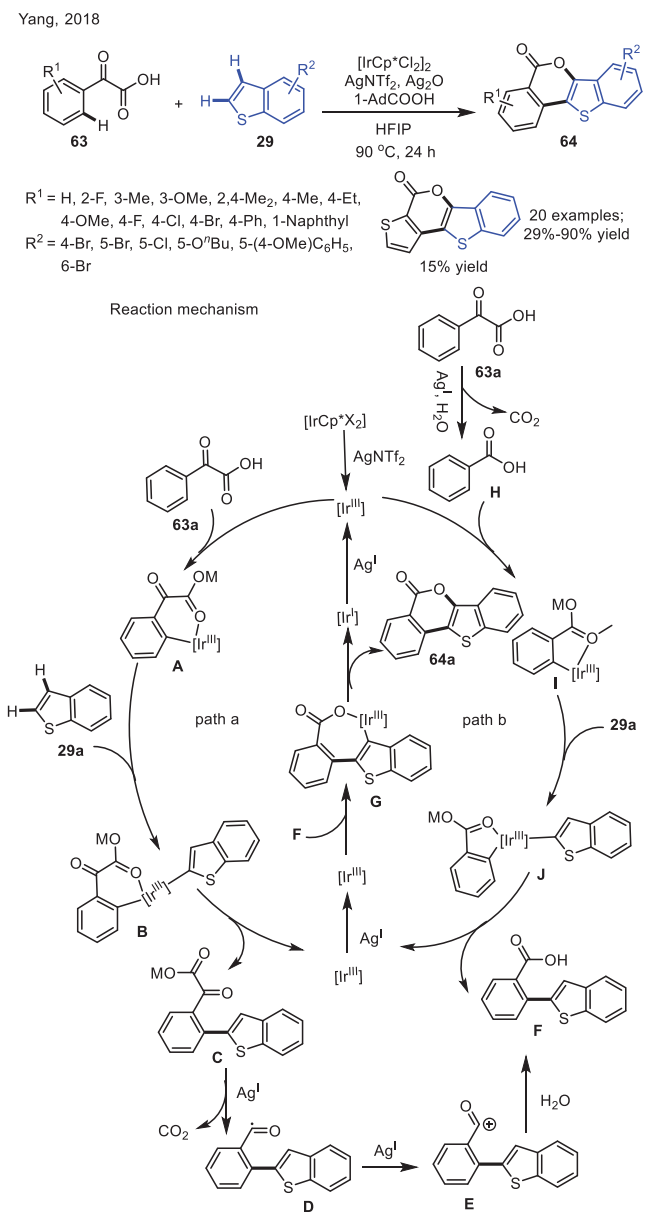
in the second step. Lastly, the resulting products underwent oxidative cycloamination to afford the target products **86** in the presence of CuCl·2LiCl.

In 2021, Doye's group developed the reaction of amines **87** with 3-bromobenzo[*b*]thiophene derivatives **88** to generate benzo[*b*]thiophene-fused 6- or 7-membered ring compounds (**89**, **90** and **91**) under three different titanium catalysts (**Cat-12** or **Cat-13** or **Cat-14**). The yields of the desired products were as high as 93% (Scheme 26) [62].

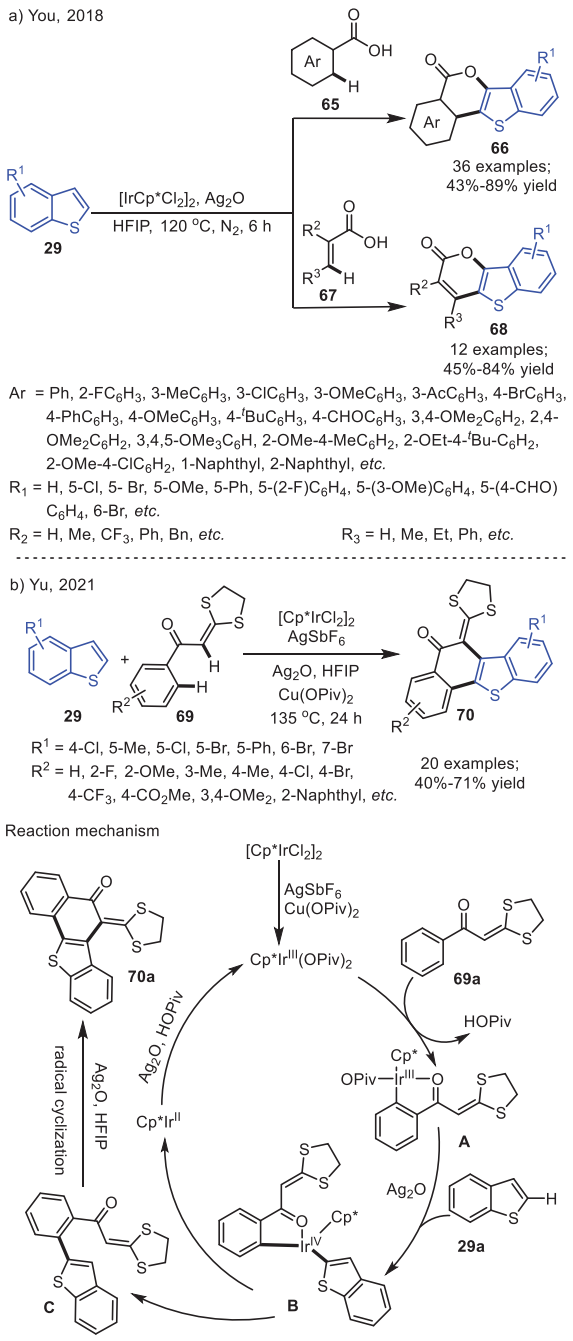
In 2015, Miura and co-workers reported a $Pd(TFA)_2$-catalyzed intramolecular coupling reaction of 3-aryloxybenzo[*b*]thiophenes **92**, which effectively constructed benzothieno[3,2-*b*]benzo-furans **93** in moderate to good yields (Scheme 27a) [63]. However, when a 2-naphthoxy group was installed on the C3 position of benzo[*b*]thiophene, the reaction produced two compounds and the yield dropped significantly. In 2015, Kuninobu and co-workers disclosed a palladium-catalyzed intramolecular oxidative C–H/C–H cross-coupling reaction of benzo[*b*]thiophene derivatives (**94** and **96**) (Scheme 27b) [64]. Benzo[*b*]thiophene fused heterocycles (**95** and **97)** with different structural types were obtained by using $[Pd(OPiv)_2]$ and AgOPiv as the catalyst and oxidant, respectively. The mechanism suggested that $[Pd(OPiv)_2]$ first reacted with **94** to give PivOH and intermediate **A**. Subsequently, a C–H bond activation transformed intermediate **A** into palladacyclic intermediate **B** with release of PivOH. Finally, intermediate **B** underwent a reductive elimination process in the presence of AgOPiv to afford the desired products **95** and regenerated $[Pd(OPiv)_2]$.

In 2017, Suga's research group developed a dehydrogenative annulation reaction for the synthesis of benzosilolothiophene derivatives **100** (Scheme 28) [65]. Under the catalysis of $[Rh(cod)Cl]_2$ and dppe-F_{20}, 2-[2-(diphenylsilyl)phenyl]benzo[*b*]-thiophene and the analogues (**98** and **99**) could be transformed into benzosilolothiophenes **100** in moderate to excellent yields.

In 2018, You's group developed a novel C–H/C–H cross-coupling reaction of *N*-methylimidazolium salts **101** with benzofuran **102** or benzo[*b*]thiophene **29**. Under the catalysis of $RhCl_3·3H_2O$, benzo[*b*]thiophene fused molecules (**103** and **104**) were successfully obtained (Scheme 29a) [66]. Experimental results indicated that both $RhCl_3·3H_2O$ and trifluoroacetic acid anhydride (TFAH) played a crucial role in this reaction. In 2019, Lan *et al.* reported the construction of benzo[*b*]thiophene-fused derivatives from by Rh(III)-catalyzed reaction of benzaldehydes **105** and benzo[*b*]thiophenes **29** (Scheme 29b) [67]. Two kinds of benzo[*b*]thiophene-fused polycyclic compounds (**106** and **108**) were obtained using *β*-alanine or **107** in HFIP at 120 °C. On the other hand, when using $BnNH_2$ in *t*-amyl alcohol (*t*-AmylOH) and/or 1,2-dichloroethane (DCE), *ortho*-benzo[*b*]thiophene benzaldehydes **109** were obtained and could be further transformed



Scheme 19. Iridium-catalyzed oxidative cyclization of phenylglyoxylic acids with benzo[*b*]thiophenes.

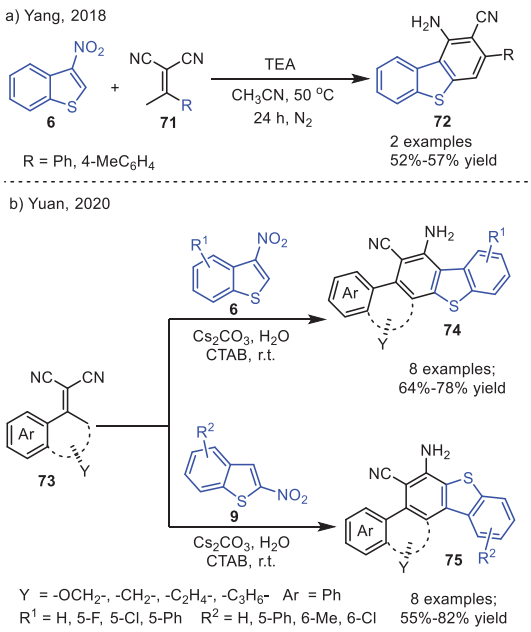


Scheme 20. Synthesis of benzo[*b*]thiophene-fused derivatives *via* Iridium catalysis.

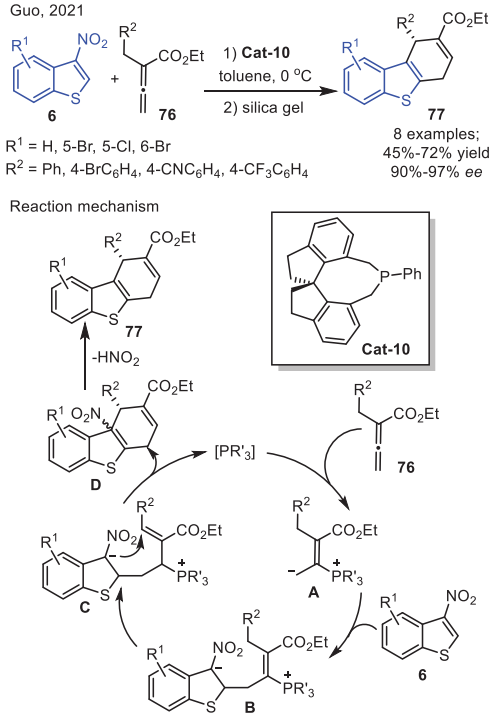
into benzo[*b*]thiophene-fused indanone derivatives **110** *via* an intramolecular dehydrogenative arylation process. The mechanism suggested that benzaldehyde **105** first reacted with RNH_2 to generate intermediate **A**, which coordinated to $Cp^*Rh^{III}L_2$ and was subsequently converted to intermediate **B** by *ortho*-C-H activation. Intermediate **B** reacted with benzo[*b*]thiophene to give intermediate **C**, followed by the formation of intermediate **D** and release of Cp^*Rh^{I} that could be converted to $Cp^*Rh^{III}L_2$ to fulfill the catalytic cycle. Intermediate **D** was finally converted to **109** when $BnNH_2$ was used in *t*-AmylOH and/or DCE, while **106** was obtained from intermediate **D** when β-alanine in HFIP was used.

In 2017, Zhu's group carried out an intramolecular C−O Ullmann reaction of 2-(3-bromobenzo[*b*]thiophen-2-yl)phenol derivatives **111** to construct benzoheterocyclic-fused core frameworks (Scheme 30) [68]. Under the catalysis of CuI and 1,10-phenanthroline, benzothieno[3,2-*b*]furan-fused heterocycles **112** were obtained in good to excellent yields (up to 97% yield).

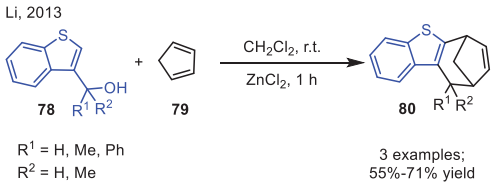
In 2020, Suga's group reported a dehydrogenative cyclization of 2-(benzo[*b*]furan-2-yl)benzenethiol derivatives **113** in the presence of $^nBu_4NBr$ (Scheme 31a) [69], providing an efficient approach for the synthesis of benzo[*b*]thiophene-fused thienoacenes **114**. In 2021, the same group further developed this type of reaction to synthesize the compounds of similar structure. Under the catalysis of $Cu(OAc)_2$, a variety of benzo[*b*]thiophene-fused furanobenzenes (**116** and **118**) were obtained (Scheme 31b) [70]. The intramolecular coupling reaction of 2-(benzo[*b*]thiophen-2-yl)phenols **115** or 2-(benzo-[*b*]thiophen-3-yl)phenols **117** in the mixed solvent of *N*-methyl-2-pyrrolidone (NMP), ethylene glycol monomethyl ether (EGM), and toluene at 145 °C under air could serve as an important synthetic route for the construction of benzo[*b*]thiophene fused heterocycles. The authors assumed that Cu species initially reacted with **115** to give intermediate **A** and carboxylic acid. *Via*



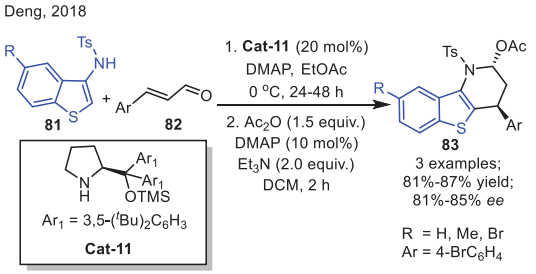
Scheme 21. Synthesis of benzo[*b*]thiophene derivatives *via* [4 + 2] annulation.



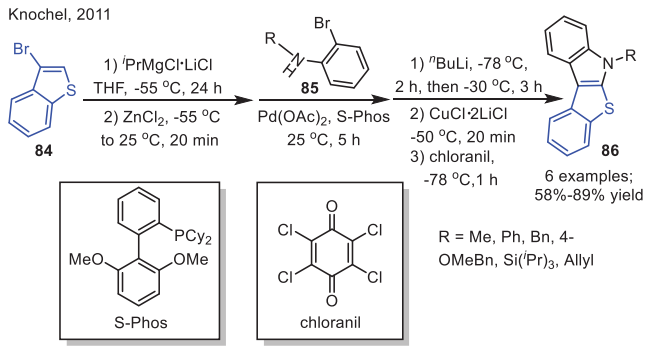
Scheme 22. Phosphine-catalyzed [4 + 2] annulation of 3-nitrobenzo[*b*]thiophene with allenoates.



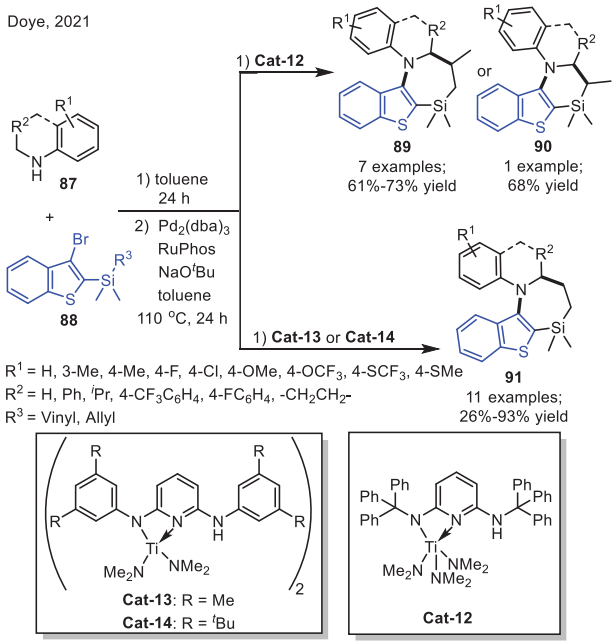
Scheme 23. Synthesis of benzo[*b*]thiophene-fused bicyclo[3.2.1]octa-2,6-dienes.



Scheme 24. Synthesis of benzo[*b*]thiophene-fused derivatives *via* [3 + 3] cycloaddition.



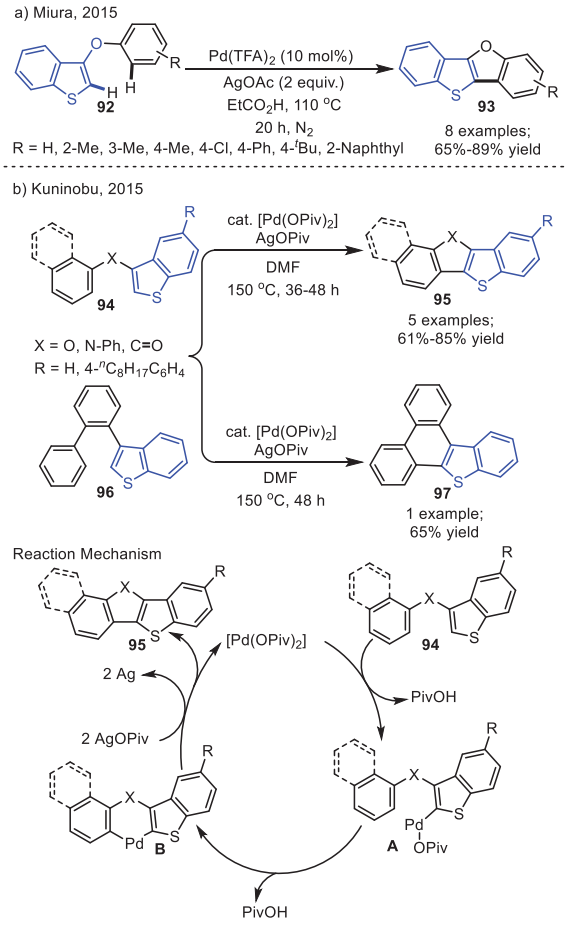
Scheme 25. The synthetic route for the preparation of benzo[4,5]thieno[2,3-*b*]indole derivatives.



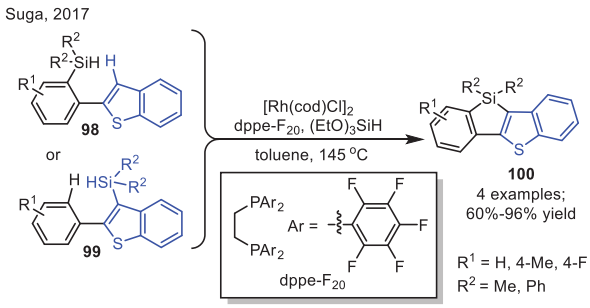
Scheme 26. The synthesis of benzo[*b*]thiophene-fused 6- or 7-membered ring compounds.

transition state **B**, the formed intermediate **A** evolved to intermediate **C** and carboxylic acid. Finally, a reductive elimination at **C** led to the formation of **116** and release of CuL_n, which could be recovered to the initial Cu species by carboxylic acid and O_2 to restart the catalytic cycles. Notably, the process from the beginning to **C** was reversible.

Metal-free methodologies have also been widely utilized to access benzoheterocycle-fused compounds in the past few years. In 2016, Ramasastry *et al.* innovatively proposed an organophosphine-

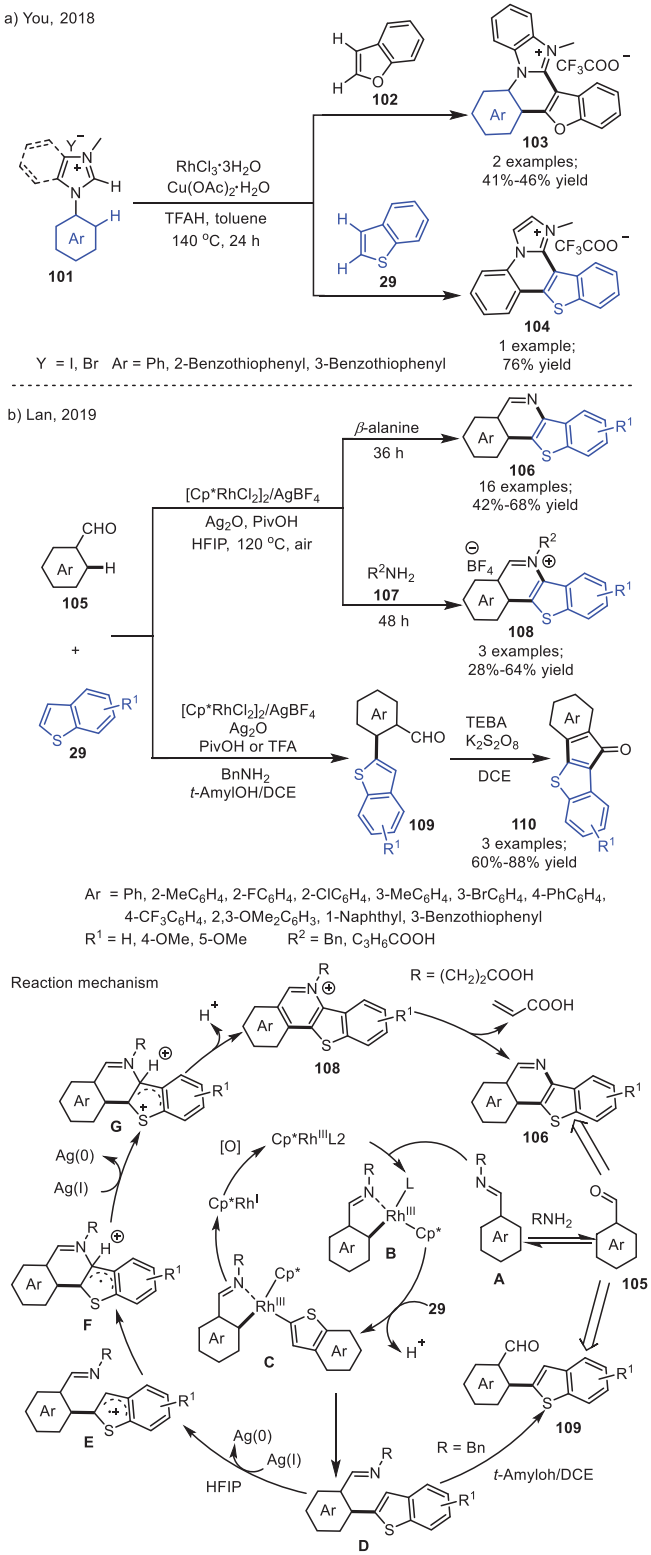


Scheme 27. Synthesis of benzo[*b*]thiophene derivatives by palladium-catalyzed coupling reaction.



Scheme 28. Rh-catalyzed synthesis of benzo[*b*]thiophene-fused derivatives.

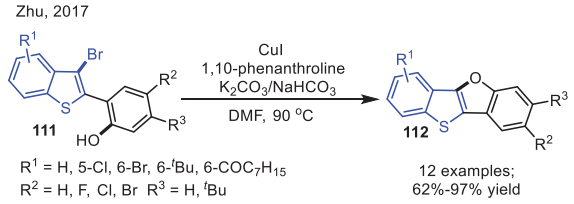
catalyzed intramolecular hydroalkylation of benzo[*b*]thiophen-3-ynones **119**. Under the catalysis of PCy_3, a range of pentannulated benzo[*b*]thiophene derivatives **120** were obtained in high yields and high stereoselectivities from benzo[*b*]thiophen-3-ynones **119** bearing different substituents (Scheme 32) [71]. The authors proposed two reaction pathways (part a and part b) to explain deuterium incorporation at the β-position and γ'-position. The results indicated that only deuterium incorporation at the γ'-position occurred during the reaction. The mechanism suggested that **119** first reacted with PCy_3 to form intermediate **A**. Deuterium incorporation at the β-position of **A** gave intermediate **B**, and then, deuterium ion attacked intermediate **B** resulting in the formation of intermediate **C**. The removal of PR_3 from **C** formed intermediate **D**, which was converted to intermediate **E** through enolization. The



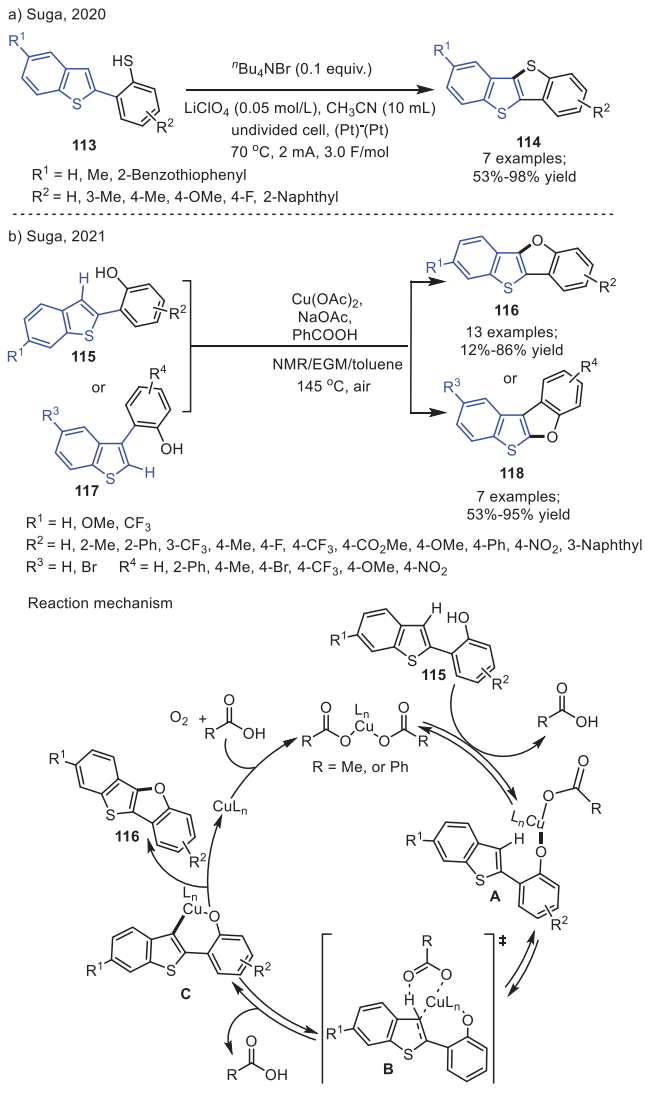
Scheme 29. Rh-catalyzed reaction leading to polycyclic benzo[*b*]thiophene-fused derivatives.

H/D exchange at the hydroxyl group by the presence of D_2O led to intermediate **F**. Finally, the desired product (**120a** or **120a'**) was obtained after deuteration of intermediate **F**.

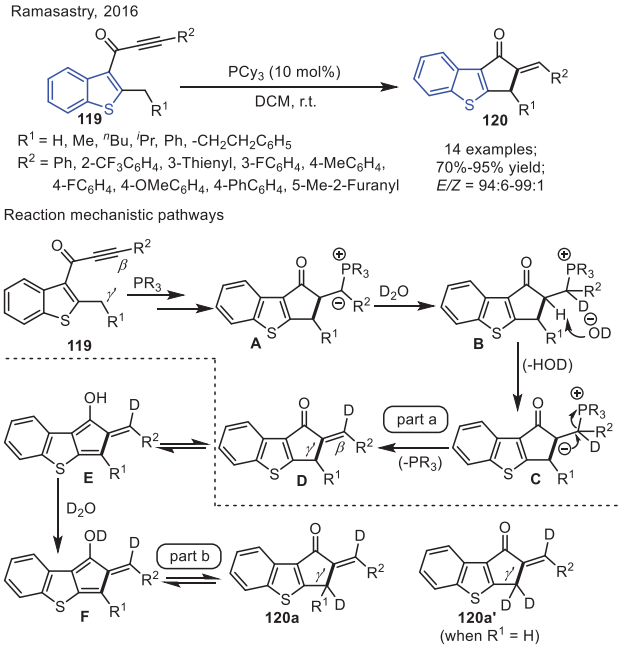
In 2019, Kitamura and co-workers developed a new strategy to synthesize [1]benzothieno[3,2-*b*][1]benzo[*b*]thiophene derivatives **114** from 1,2-bis(2-methylthiophenyl)-ethynes **121**.



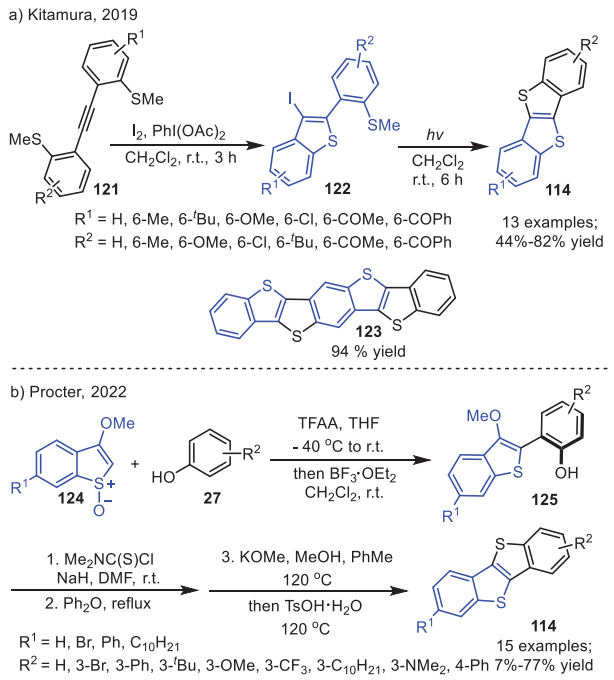
Scheme 30. Synthesis of benzothieno[3,2-*b*]furan-fused heterocycles *via* intramolecular C–O Ullmann reaction.



Scheme 31. Dehydrogenative cyclization of benzo[*b*]thiophene derivatives.



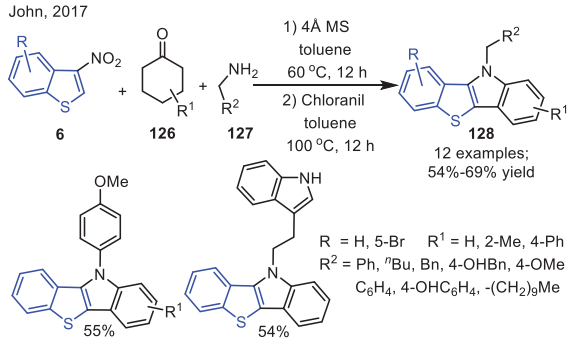
Scheme 32. PCy_3-catalyzed intramolecular hydroalkylation of benzo[*b*]thiophen-3-ynones.



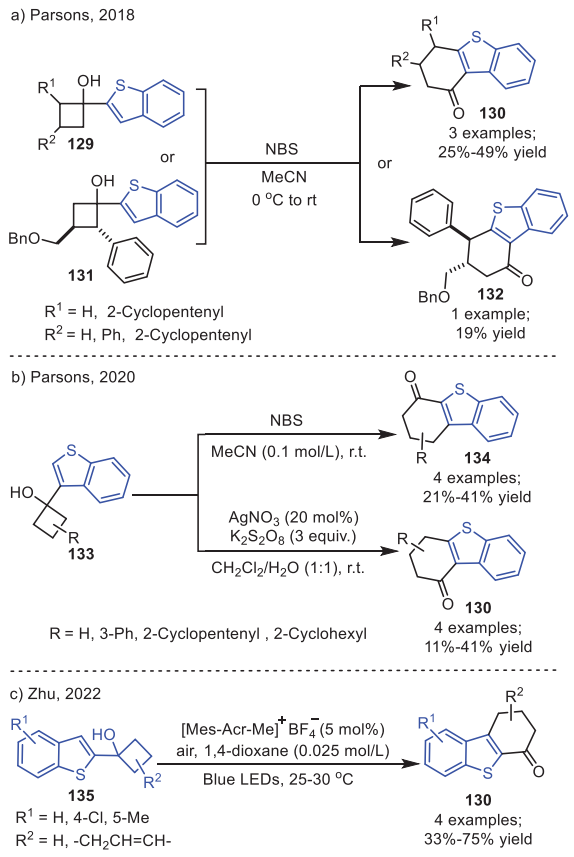
Scheme 33. Synthesis of [1]benzothieno[3,2-*b*][1]benzo[*b*]thiophene derivatives.

In this method, 1,2-bis(2-methylthiophenyl)-ethynes **121** were first converted to 3-iodo-(2-methylthiophenyl)benzo[*b*]thiophenes **122** in the presence of I_2 and $PhI(OAc)_2$ at room temperature, which then underwent a photolysis reaction to generate [1]benzothieno[3,2-*b*][1]benzo[*b*]thiophene derivatives **114**. At the same time, bis[1]benzothieno[2,3-*d*;2′,3′-*d*′]benzo[1,2-*b*;4,5-*b*′]dithiophene **123** was also obtained in high yield (94%) (Scheme 33a) [72]. In 2022, Procter *et al.* also reported a synthetic method to access [1]benzothieno[3,2-*b*][1]benzo[*b*]thiophene derivatives **114** (Scheme 33b) [73] through three processes. Under the catalysis of trifluoroacetic anhydride (TFAA), benzo[*b*]thiophene *S*-oxides **124** and phenols **27** first underwent a Pummerer CH–CH-type cross coupling reaction to form 2-(3-methoxybenzo[*b*]thiophen-2-yl)phenols **125**, which were further transformed through a Newmann-Kwart reaction. The final cyclization process afforded the desired products **114**. These reactions provided a useful route for the synthesis of bisbenzo[*b*]thiophene skeleton compounds.

In 2017, John and co-workers described an efficient method for the preparation of benzothieno[3,2-*b*]indoles **128** *via* a metal-free, one-pot three-component reaction of 3-nitrobenzo[*b*]thiophene **6**, cyclohexanones **126** and primary amines **127** (Scheme 34) [74]. By means of this approach, various benzothieno[3,2-*b*]indoles **128** were obtained in satisfactory yields.

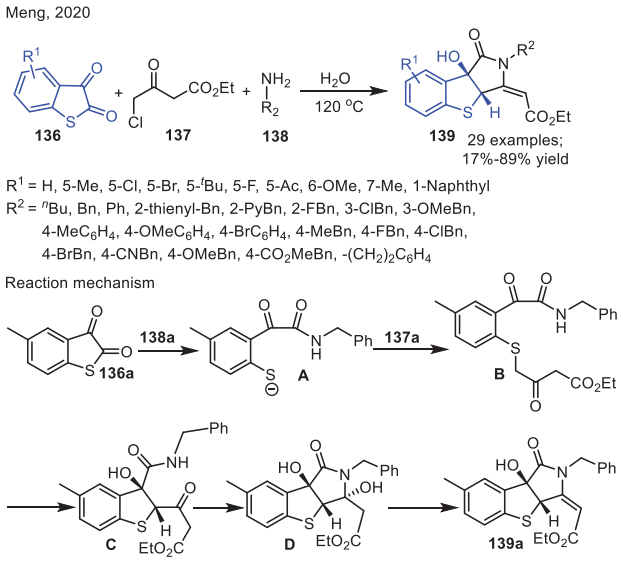


Scheme 34. The three-component reaction of 3-nitrobenzo[*b*]thiophene, cyclohexanones, and primary amines.



Scheme 35. Synthesis of tetralone derivatives *via* ring expansion reactions.

To overcome the difficulty in the synthesis of tetralones, Parsons's group developed an efficient approach to access 4-tetralones (**130** and **132**) by a transition-metal-free ring expansion of 1-(benzo[*b*]thiophen-2-yl)cyclobutan-1-ol derivatives (**129** and **131**) in 2018 (Scheme 35a) [75]. The reaction was carried out under mild conditions with commercially available reagents *N*-bromosuccinimide (NBS) and CH_3CN. In 2020, the same research group further discovered that 4-tetralones **130** could be synthesized from 1-(benzo[*b*]thiophen-3-yl)cyclobutan-1-ols **133** by $AgNO_3$-mediated ring expansion reaction. Moreover, the 1-(benzo[*b*]thiophen-3-yl)cyclobutan-1-ols **133** could also be converted to 1-tetralones **134** upon NBS-mediation, which provided a feasible method for the synthesis of different tetralone derivatives (Scheme 35b) [76]. In 2022, Zhu's group found that benzo[*b*]thiophene-substituted cyclobutanols **135** could be converted to 1-tetralones **130** in the presence of $[Mes\text{-}Acr\text{-}Me]^+BF_4^-$



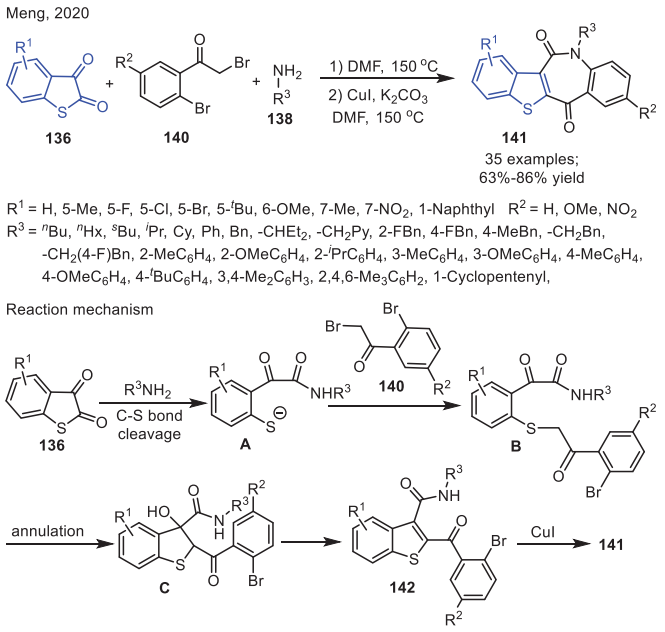
Scheme 36. Synthesis of benzo[*b*]thiophene-fused pyrrolidone derivatives by three-component domino reaction.

and 1,4-dioxane (Scheme 35c) [77]. This reaction provided a facile way to access tetralones to afford the desired products **130** in moderate to good yields at air atmosphere.

3. Synthesis of benzo[*b*]thiophene fused cyclic compounds from benzo[*b*]thiophene-2,3-diones and their analogues

Thioisatin has broad application prospects in the synthesis of sulfur-containing heterocyclic compounds. In recent years, our research group have made great progress in the construction of benzo[*b*]thiophene fused heterocyclic compounds from thioisatin. In 2020, we developed an efficient approach for the synthesis of benzo[*b*]thiophene fused pyrrolidone derivatives **139**. This method proceeded through an eco-friendly, nontoxic three-component domino reaction of thioisatins **136**, ethyl 4–chloro-3-oxobutanoate **137** and amines **138** in water, successfully obtaining a wide variety of benzo[*b*]thiophene fused pyrrolidone derivatives **139** (Scheme 36) [78]. The mechanism suggested that amine **138a** initially attacked on the C2 position of **136a** to form intermediate **A**. Then, **A** reacted with **137a** to produce intermediate **B**, followed by an intramolecular nucleophilic addition to give intermediate **C**. Afterwards, intermediate **D** was generated by a *N*-nucleophilic addition. Finally, **D** underwent dehydration to form benzo[*b*]thiophene fused pyrrolidone derivative **139a**.

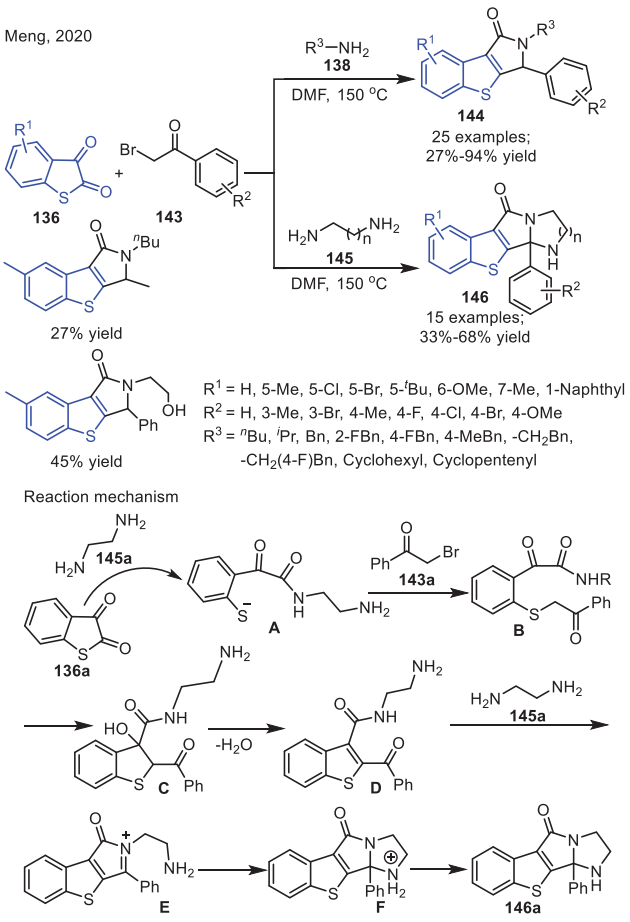
In 2020, we proposed a synthetic method for the preparation of benzothiopheno[2,3-*e*]azepinedione derivatives **141** from thioisatins **136**, *ortho*-Br α-bromoketones **140** and amines **138** by a three-component reaction (Scheme 37) [79]. This reaction was found to have a wide substrate range and high overall product yields (>63%). However, when α-bromoketones **143** were used instead of *ortho*-Br α-bromoketones **140**, the desired benzo[*b*]thiophene fused seven-membered ring compounds **141** were not obtained and another benzo[*b*]thiophene derivatives **142** were obtained. The plausible mechanism was very similar to that of the reaction of thioisatins **136** with ethyl 4–chloro-3-oxobutanoate **137** and amines **138** (Scheme 36). The difference was that intermediate **C** underwent a dehydration reaction to give compound **142**, and the latter species needed to be catalyzed by CuI under the premise that the substrate could only be *ortho*-Br α-bromoketones **140** to generate benzo[*b*]thiophene fused heterocycles **141**.



Scheme 37. Synthesis of benzothiopheno[2,3-*e*]azepinedione derivatives by three-component reaction.

In the same year, our group reported that α-bromoketones **143** could be combined with thioisatins **136** and amines (**138** and **145**) to synthesize benzo[*b*]thiophene fused *N*-heterocycles **144** and benzo[*b*]thiophene-fused *N*-polyheterocyclic compounds **146** through a three-component domino reaction in DMF instead of H_2O (Scheme 38) [80]. The highest yield of the target product could reach up to 94%. On the proposed reaction pathway, thioisatin **136a** initially reacted with amine **145a** to form intermediate **A**, which was followed by reaction with 2–bromo-1-phenylethan-1-one **143a** to give intermediate **B**. An intramolecular cyclization of **B** constructed a five-membered ring to deliver intermediate **C**. Then, intermediate **C** was converted to intermediate **D** by dehydration, which reacted with another amine to generate intermediate **E**. An intramolecular nucleophilic addition transformed intermediate **E** into **F**. Finally, the desired benzo[*b*]thiophene-fused *N*-polyheterocyclic compound **146a** was produced after deprotonation of **F**.

In the subsequent work, we further extended the three-component domino reaction of thioisatins **136** with α-bromoketones **143** and amines. It was found that benzo[*b*]thiophene-fused polycyclic compounds **148** and benzo[*b*]thiophene-fused eight-membered *N*-heterocycles **149** were obtained by using two types of tryptamines **147** to react with thioisatins **136** and α-bromoketones **143** in DMF at 150 °C (Scheme 39) [81]. The generality and practicability of this reaction have been verified by gram scale experiments and transformation experiments. The mechanism showed that thioisatin **136** initially reacted with tryptamine **147a** to form intermediate **A**, which was followed by reaction with α-bromoketones **143a** to give intermediate **B**. An intramolecular cyclization delivered intermediate **C**, and the following dehydration process generated intermediate **D**. When R^3 = H, intermediate **D** was converted to intermediate **E**. Finally, benzo[*b*]thiophene-fused polycyclic compound **148a** was formed from **E**. However, When R^3 = CO_2Me, the conversion of intermediate **C** to **F** took place, possibly due to the influence of steric hindrance. Subsequently, intermediate **F** was transformed into intermediate **G**, followed by decarbonylation to generate intermediate **H**. Finally, benzo[*b*]thiophene-fused eight-membered *N*-heterocycle **149a** was produced by dehydration of **H**.

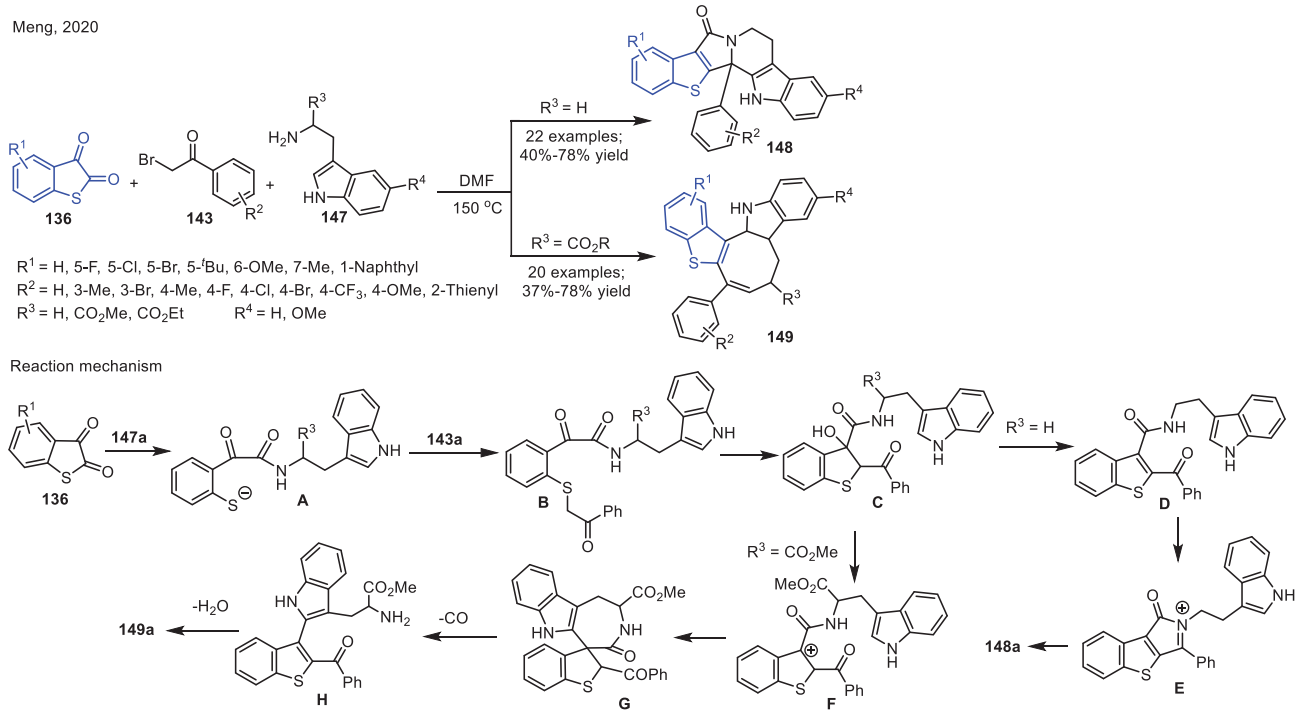


Scheme 38. Synthesis of benzo[*b*]thiophene fused *N*-heterocycles by three-component domino reaction.

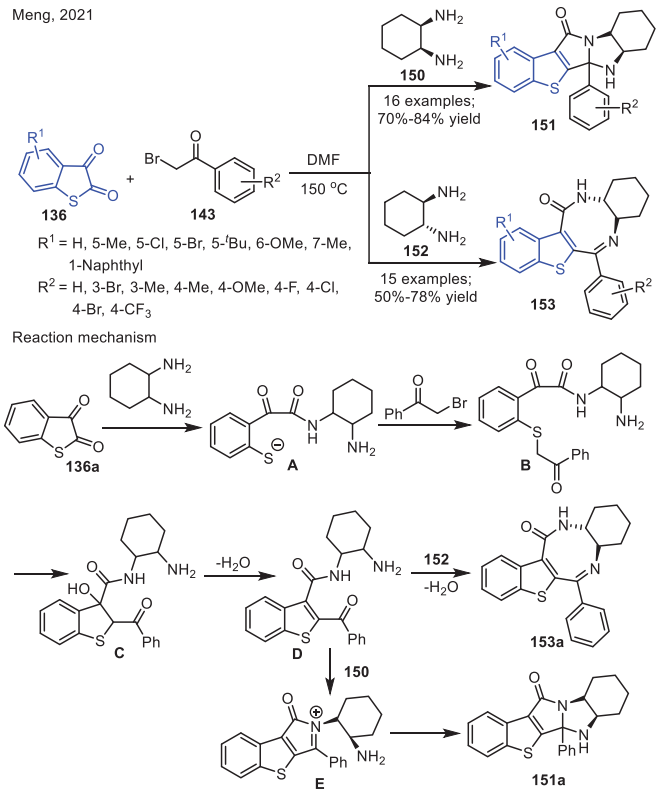
In 2021, we reported a stereo-tunable domino reaction of thioisatins **136** with α-bromoketones **143** and cyclohexane1,2-diamines (**150** and **152**) (Scheme 40) [82]. The desired products **151** or **153** could be selectively obtained by using cyclohexane1,2-diamines with different stereo configurations (**150** and **152**). In the reaction mechanism, the processes from thioisatin to intermediate **D** were similar to the reaction mechanism of thioisatins **136** and α-bromoketones **143** with amines (**138** and **145**) (Scheme 38), but the processes after intermediate **D** were different. With the use of **152**, benzo[*b*]thiophene fused eight-membered *N*-heterocycle **153a** was formed. In contrast, the use of **150** facilitated the transformation of intermediate **D** into **E**, which was converted to benzo[*b*]thiophene-fused polycycle **151a**. As another approach to access benzoheterocycle-fused compounds, the domino reaction between thioisatins **136** and α-bromoketones **143** was reported by our research group in 2021 (Scheme 41) [83]. This approach was simple and versatile, and what's more, and the high selectivity for the formation of two types of sulfur-containing heterocyclic compounds (**154** and **155**) was easily controlled by the presence or absence of $MgSO_4$. By using $MgSO_4$ and K_2CO_3 at CH_3CN in reflux situation, the reaction successfully afforded a series of benzo[*b*]thiophene fused pyranones **154** in good to excellent yields (up to 95% yield).

4. Synthesis of benzo[*b*]thiophene fused cyclic compounds from (*Z*)-benzylidenebenzo[*b*]thiophen-3(*2H*)-ones and their analogues

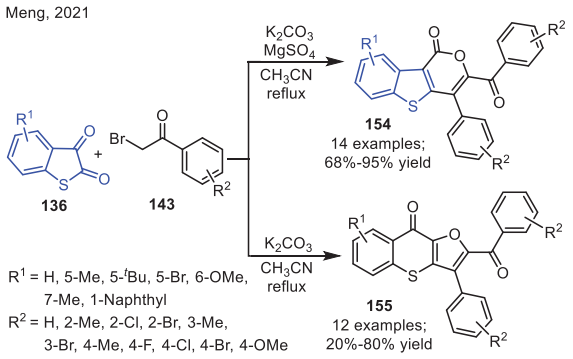
As central building blocks of benzo[*b*]thiophene condensates, thioaurones can undergo cyclization reaction with a variety of



Scheme 39. Synthetic route to benzo[*b*]thiophene-fused polycyclic compounds and benzo[*b*]thiophene-fused eight-membered *N*-heterocycles.



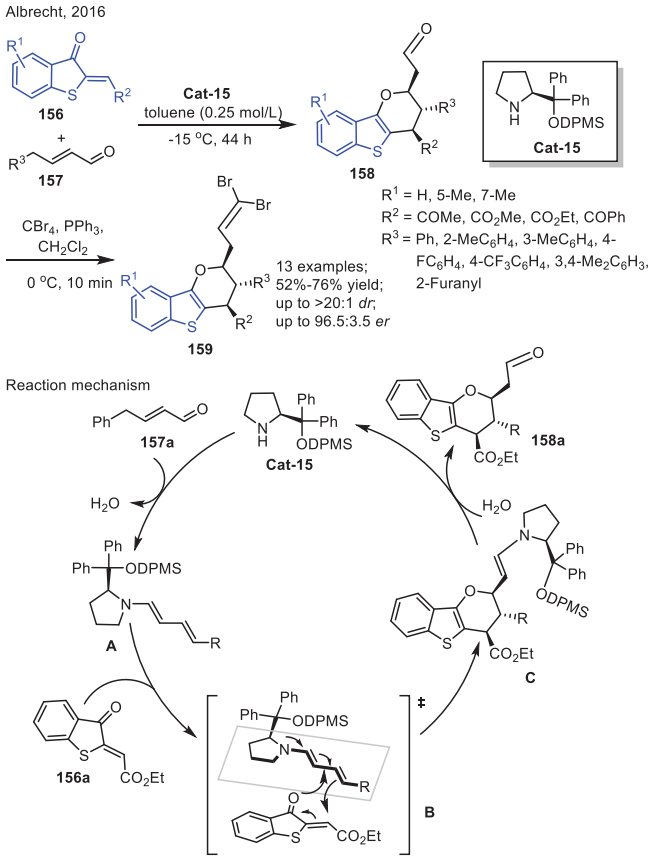
Scheme 40. Approach to the synthesis of benzo[*b*]thiophene-fused heterocyclic derivatives.



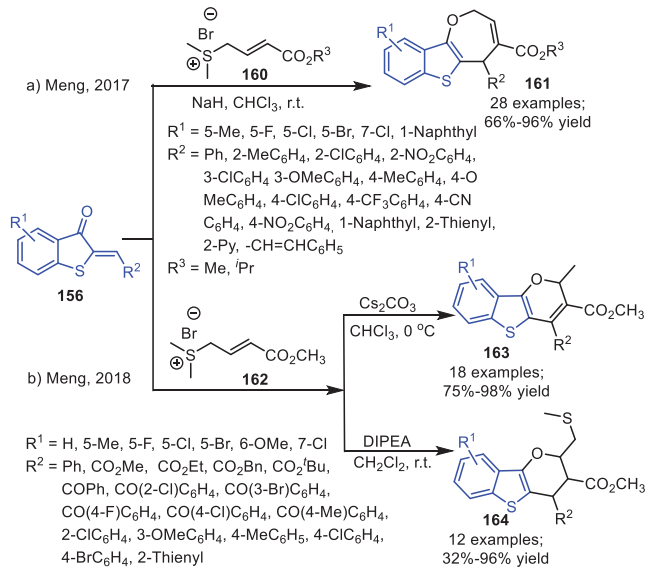
Scheme 41. The domino reaction between thioisatins and α-bromoketones.

organic compounds, and the produced benzo[*b*]thiophene derivatives have many important applications in different fields. In 2016, Albrecht's research group reported a [4 + 2] cyclization between 2-alkylenebenzo[*b*]thiophene-3(2*H*)-ones **156** and dienamines **157** (Scheme 42) [84]. Thioaurones were used as heterodienes for the synthesis of benzo[*b*]thiophene skeletons, and the enantioselectivity was based on the principle of steric shielding by utilizing the particular amino catalyst **Cat-15**. The mechanism showed that **Cat-15** was first condensed with unsaturated aldehyde **157a**, together with deprotonation and isomerization, to provide dienamine **A**. Then, the [4 + 2] reaction between **B** and **156a** occurred *via* transition state **B** to generate enamine **C**, and the *s-cis* conformation of **156a** was fixed. The final hydrolysis yielded the desired product **158a**.

In 2017, our group investigated the reaction between thioaurones **156** and sulfur ylide **160**. Using NaH as the catalyst, [4 + 3] cyclization occurred to delivered the products **161** in high yields (Scheme 43a) [85]. In 2018, we conducted an in-depth study by using different catalysts in the domino reaction of thioaurones **156** with sulfur ylide **162** (Scheme 43b) [86]. In this work, sulfur ylide was used as a two-carbon synthon to engage in a [4 + 2] cyclization with thioaurone. The products **163** containing a pyran ring were generated under the catalysis of Cs_2CO_3, while the products **164** were generated under the catalysis of *N,N*-Diisopropylethylamine (DIPEA).

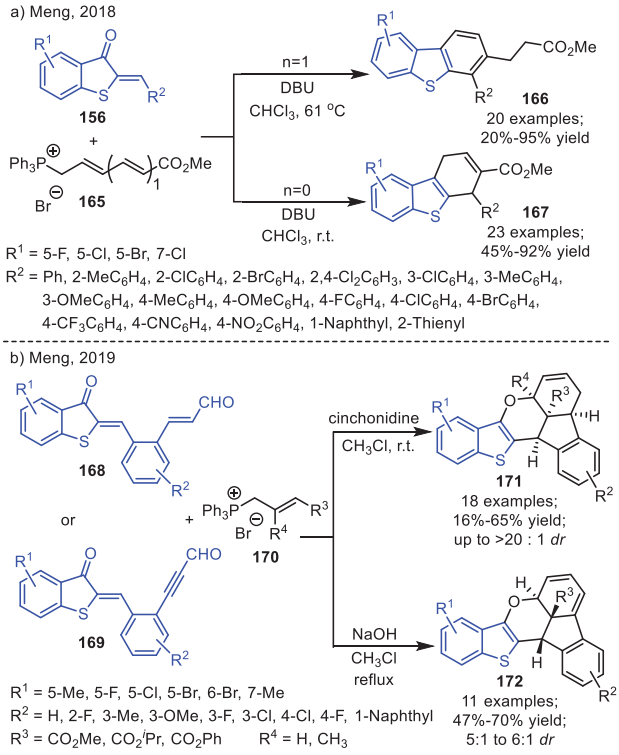


Scheme 42. The cycloaddition of thiouranone to dienamines.



Scheme 43. Cyclization of thioherones with allyl thiylides on different carbon atoms.

In the same year, we also studied the domino reaction between thioaurones **156** and phosphorus ylides **165**, with the latter species being similar to allyl sulfur ylides (Scheme 44a) [87]. As compared to sulfur ylides, the phosphorus ylides with different conjugation lengths were investigated. Although the same [3 + 3] cyclization occurred, the resulting products **166** and **167** were different. In

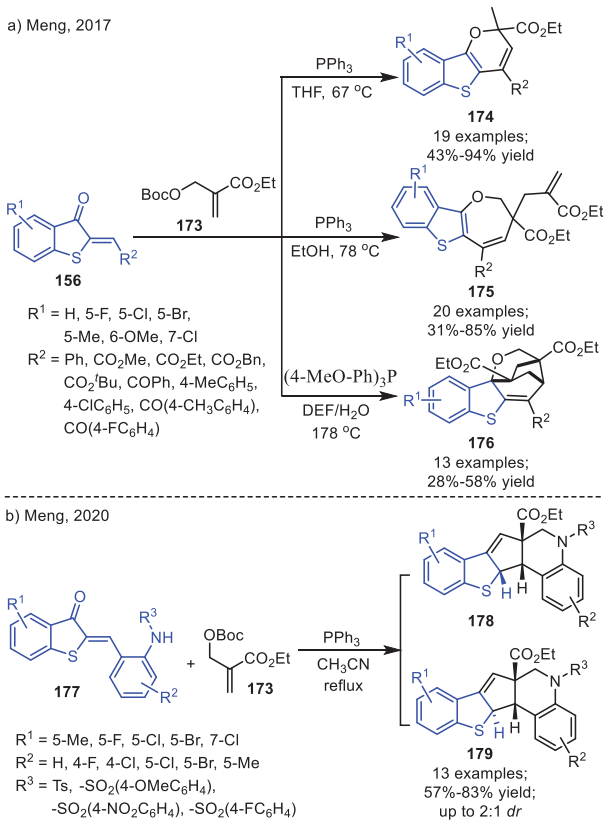


Scheme 44. Research on thiourea ketones and allyl phosphorus ylides.

2019, we employed cinchonidine or NaOH to promote the reaction of thioaurones with phosphorus ylides to form benzo[*b*]thiophene fused tricyclic backbone (Scheme 44b) [88]. When thioaurones (**168** and **169**) containing *a,β*-unsaturated aldehydes were used to react with phosphorus ylides **170** by different base catalysts, the umbrella-shaped oxatricycles **171** and **172** with high stereoselectivity were obtained in good yields.

In 2017, we explored the reaction of thioaurones **156** with MBH carbonate **173** (Scheme 45a) [89]. In this work, different solvents were screened to control the domino reaction. The benzo[*b*]thiophene-fused pyran derivatives **174**, the oxacyclic cycloheptadienes **175** and the oxatricyclodecene compounds **176** were obtained by using THF, EtOH, and *N,N*-diethylformamide (DEF)/H_2O as solvent, respectively. In 2020, we expanded our research to thioaurones **177** and MBH carbonate **173** (Scheme 45b) [90] and disclosed a novel phosphorus-catalyzed domino reaction. The benzo[*b*]thiophene fused [6–5–5–6–6] pentacyclic skeleton was constructed using PPh_3 as catalyst, and **178** and **179** were obtained with different stereoselectivities.

In 2018, we performed a [4 + 2] annulation of thioaurones **156** and benzyl allenoates **180** (Scheme 46a) [91]. The benzothieno[3,2-*b*]pyran derivatives **181** were obtained by refluxing in toluene under the efficient catalysis of tris(4-methoxyphenyl)phosphorus. In the same year, we investigated the domino reaction of thioaurones **182** with allenoate **183** (Scheme 46b) [92]. A series of bridged bicyclic benzo[*b*]thiophene-fused dioxabicyclo[3.3.1]nonane derivatives **184** were obtained in the presence of tris(4-methoxyphenyl)phosphorus catalyst. In 2019, we further studied the tandem reaction of thiouranones **156** with allenoate **183** (Scheme 46c) [93]. Using DABCO as the catalyst of the [4 + 2] cyclization, two different benzo[*b*]thiophene derivatives **185** and **186** were obtained in good yields. In the same year, Veselý's group developed a cycloaddition reaction of 3-alkylidene benzo[*b*]thiophenes **187** with allenoates **188** (Scheme 46d) [94]. By the use of quinidine **Cat-16** as catalyst and 2,4-dinitrobenzoic acid



Scheme 45. Research on the correlation between thiourea ketones and MBH carbonates.

(2,4-DNBA) as additive, benzo[*b*]thiophene derivatives **189** and **190** were produced in high yields and high enantioselectivities.

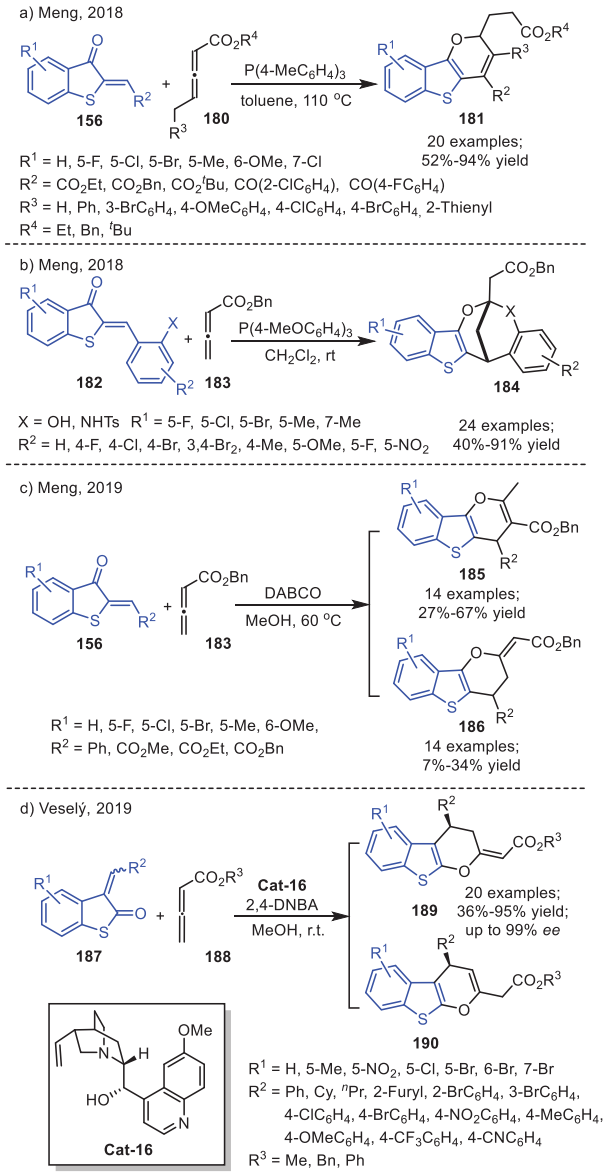
In 2019, our group explored the piperidine-catalyzed reaction of thioaurones **156** and nitrile compounds **191** at room temperature to form benzo[*b*]thiophene-fused pyran derivatives **192** (Scheme 47) [95].

In the same year, Albrecht and co-workers proposed the synthesis of benzo[*b*]thiophene-fused derivatives **195** through a hetero-Diels-Alder cycloaddition of thioaurones **156** with azlactones **193**. Under the catalysis of *N*-methylmorpholine **194**, a series of benzo[*b*]thiophene-fused derivatives **195** were obtained in moderate to good yields (Scheme 48) [96]. The reaction mechanism showed that azlactone **193** was first deprotonated by the Bronsted base catalyst and then underwent a Diels-Alder reaction with thioaurones **156** to generate intermediate **B**, which was followed by a ring-opening process to form intermediate **C**. Finally, intermediate **C** gave the target product **195** *via* an epimerization process.

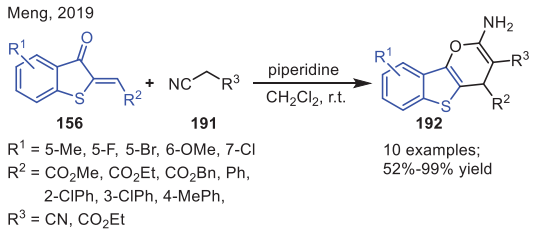
In 2022, Yuan and co-workers developed a [4 + 2] cycloaddition of 1-thioaurones **156** with γ-deconjugated butanolides **196** or azlactones **193**. A series of benzo[*b*]thiophene-fused δ-lactones (**197** and **198**) were obtained with excellent *dr* and high *ee* under the catalysis of **Cat-17**, and gram scale experimental results (70% yield, 87:13 *dr* and 99% *ee*) demonstrated the practicality of this reaction (Scheme 49) [97].

5. Synthesis of benzo[*b*]thiophene fused cyclic compounds from azadienes bearing a benzo[*b*]thiophene moiety and their analogues

In 2019, Chen *et al.* disclosed the synthesis of benzothienopyridine derivative **201** by cyclization of 1-azadienes **199** and α-

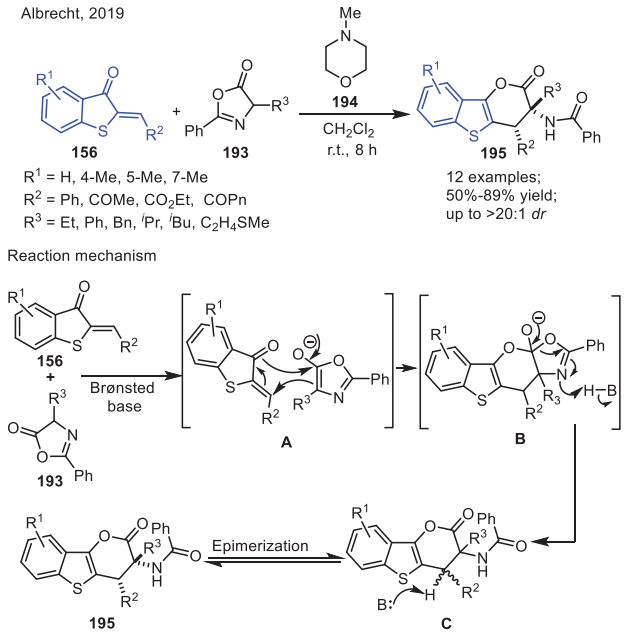


Scheme 46. Research on the reaction of thioaurones with allenoic acid esters.

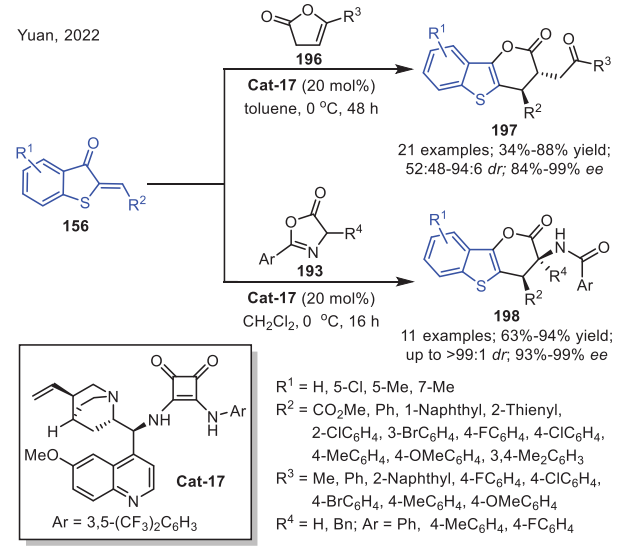


Scheme 47. Research on thioaurones and nitrile compounds.

bromoacetate **200** in a [4 + 1 + 1] fashion (Scheme 50a) [98]. In the presence of DABCO and Cs_2CO_3, the reaction proceeded smoothly in CH_3CN at 40 °C for 72 h to produce the expected benzothienopyridine derivatives. In the same year, Moreau *et al.* investigated the polycyclization of azadiene **199** with dienal **202** (Scheme 50b) [99]. The intricately fused hexacyclic unsaturated imine **203** was obtained in a highly diastereoselective manner by stirring HFIP in 37%



Scheme 48. Synthesis of benzo[*b*]thiophene-fused derivatives *via* hetero-Diels-Alder cycloaddition.

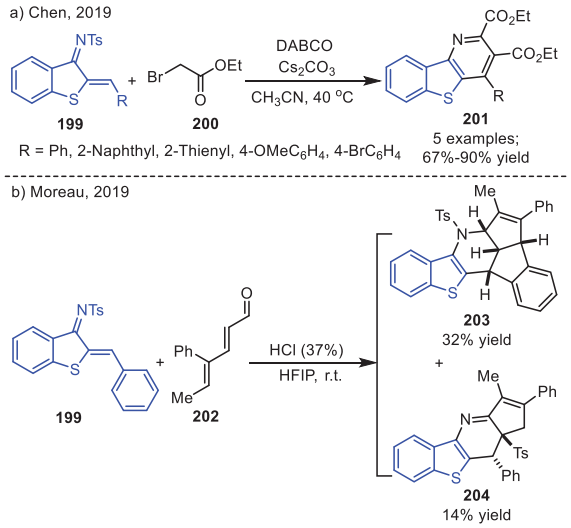


Scheme 49. **Cat-17**-catalyzed synthesis of benzo[*b*]thiophene-fused δ-lactones.

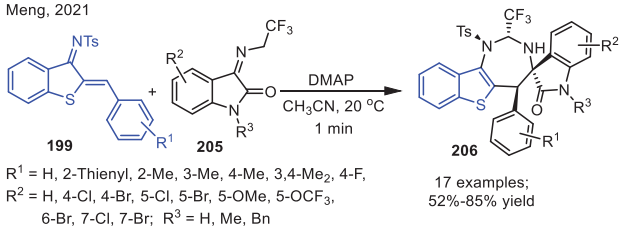
HCl at room temperature. At the same time, a rearranged product **204** was also observed and further rationalized by DFT calculation.

In 2021, our group disclosed the [4 + 3] cyclization between azadienes **199** and isatin-derived α-(trifluoromethyl)imines **205** (Scheme 51) [100] by using DMAP as the catalyst in CH_3CN at 20 °C. The condensed compounds **206** with a benzo[*b*]thiophene aza seven-membered ring were obtained.

In 2020, Chen *et al.* investigated the asymmetric regioselective [4 + 3] cyclization of azadienes **199** with isatin-derived MBH carbonates **207** by a chiral catalyst (Scheme 52a) [101]. Under the catalysis of **Cat-18**, simultaneously at 4 Å MS in the presence of toluene, the reaction took place at room temperature to furnish the chiral azepanespirooxindole compounds **208** in high yields and excellent enantioselectivities. In 2021, Chen's group turned to study



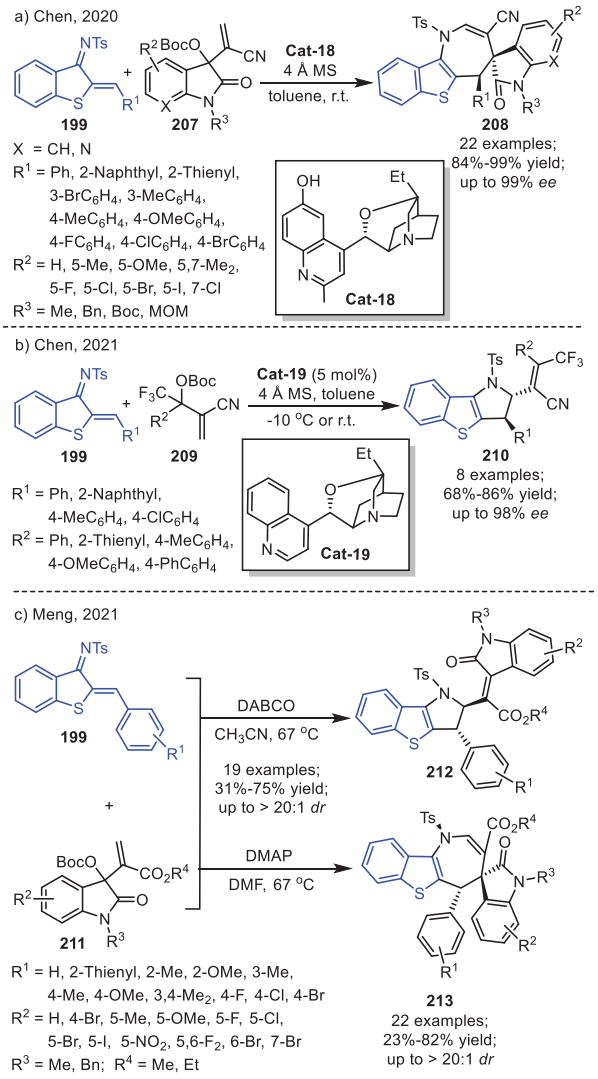
Scheme 50. Synthesis of benzo[*b*]thiophene-fused nitrogen heterocycles.



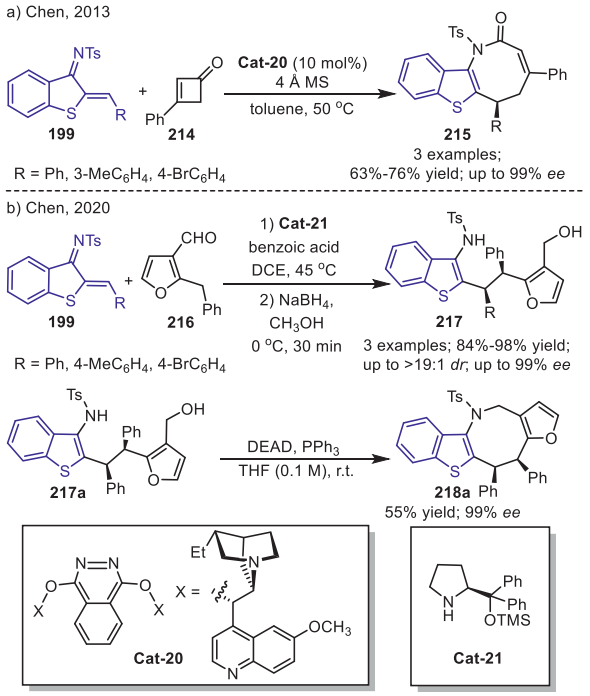
Scheme 51. The [4 + 3] cyclization of azadienes with indoloisatinimines.

the [4 + 1] cyclization of azadienes **199** with trifluoromethyl ketone and acrylonitrile derived MBH carbonates **209** under amine catalyst (Scheme 52b) [102]. With the use of the tertiary amine chiral catalyst **Cat-19**, the expected products **210** were obtained in good yields and excellent enantioselectivities at −10 °C to room temperature in toluene solution in the presence of 4 Å MS. In the same year, our group also carried out the switchable domino reaction of azadienes **199** and isatin-derived MBH carbonates **211** under catalyst-control condition (Scheme 52c) [103]. The [4 + 1] cyclization was initiated in CH_3CN at 67 °C using DABCO as the catalyst. The benzo[*b*]thiophene fused pyrrole derivatives **212** were obtained in moderate yields and higher *dr* values. The [4 + 3] cyclization was also initiated under the catalysis of DMAP in DMF at 67 °C to give benzothienoazepine derivatives **213**.

In 2013, Chen *et al.* investigated the asymmetric cyclization of 1-azadiene **199** with cyclobutanone **214** (Scheme 53a) [104]. 4 Å MS was added in toluene solvent at 50 °C under the catalysis of **Cat-20** modified cinchona alkaloids. The benzo[*b*]thiophene-fused eight-membered structure **215** was successfully constructed in good yields and remarkable enantioselectivities. Chen's group further studied the reaction of 1-azadiene in 2020. Under the catalysis of the chiral amine catalyst **Cat-21** and in the presence of 20% mol benzoic acid solution, 1-azadiene **199** underwent an asymmetric Michael addition with arylaldehyde **216** (Scheme 53b) [105]. The γ-regioselective products **217** were isolated in excellent yields with high diastereoselectivities and enantioselectivities. Then, under catalysis of diethyl azodicarboxylate (DEAD) and PPh_3 in 0.1 mol/L THF solution environment, the eight-membered ring benzo[*b*]thiophene fused derivative **218a** was obtained in a satisfactory yield and high enantioselectivity.



Scheme 52. Cyclizations of azadienes and MBH carbonates.



Scheme 53. Synthesis of benzo[*b*]thiophene fused eight-membered ring compounds from azadienes.

6. Conclusions

Sulfur-containing organic compounds, especially those bearing a benzo[*b*]thiophene skeleton, play a vital role in organic photoelectric chemistry and biologically active compounds. The past decade has witnessed the rapid development in the construction of these skeletons. This review summarized a series of efficient reactions reported in recent years for the synthesis of benzo[*b*]thiophene-fused compounds from thioaurone, thioisatin, substituted benzo[*b*]thiophene, and azadiene. A few of these reactions were developed by our group. Despite the progress achieved in this field, some problems remained to be unsolved: (1) The role of sulfur atom in governing the reactivity and/or selectivity has not been deeply understood until now. (2) Efficient strategies for the preparation of sulfur-containing π-extended polyaromatic hydrocarbons need to be broadened. (3) From the perspective of sustainable chemistry, green and economical strategies for the synthesis of benzo[*b*]thiophene fused compounds have been relatively deficient. (4) The applications of benzo[*b*]thiophene fused compounds are relative limited. Hence, it is still demanded to further develop new strategies to construct benzothiophene fused heterocycles. Firstly, the mechanism and origin of the special effects of sulfur atom need to be clarified to rationally control the expected reactivity and/or selectivity. Secondly, more efficient and greener strategies for the preparation of valuable benzo[*b*]thiophene fused compounds need to be exploited. Thirdly, we need to broaden the scope of potential applications of benzo[*b*]thiophene fused compounds to other areas. We hope this review will draw attention of chemists to achieve more advances on the construction of benzo[*b*]thiophene fused heterocycles in future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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