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The involvement of the trisulfur radical anion in electron-catalyzed sulfur insertion reactions: facile synthesis of benzothiazine derivatives under transition metal-free conditions†

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An efficient and practical synthesis of benzothiazine by K_2S initiated sulfur insertion reaction with enaminones *via* electron catalysis is developed. This protocol provides a new, environment-friendly and simple strategy to construct benzothiazine derivatives *via* formation of two C–S bonds under transition metal-free, additive-free and oxidant-free conditions. K_2S not only provides the sulfur insertion source, but also ignites the reaction through the formation of a trisulfur radical anion and electrons in DMF.

Organosulfur heterocycles have been widely used as functional materials, pharmaceuticals, and synthetic intermediates. 1,4-Benzothiazine derivatives are present in natural products, biologically relevant compounds, and other functional molecules (Fig. 1).[1] During the past decade, a number of new synthetic protocols for 1,4-benzothiazine construction based on transition metal-catalyzed reactions have been well developed.[2] The development of new methods to construct 1,4-benzothiazine derivatives *via* C–S bonds formation under transition metal-free conditions is highly desirable.

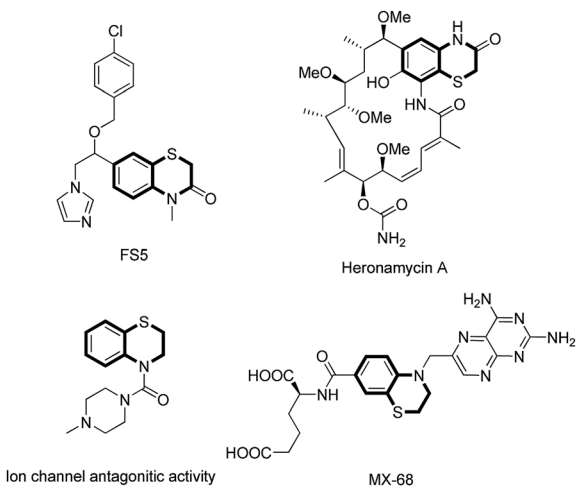
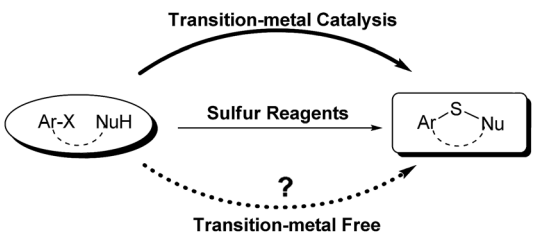


Fig. 1 Representative bioactive 1,4-benzothiazine derivatives.

Sulfur-centered radicals such as thiyl radicals and sulfonyl radicals ($RSO_2^{\bullet}$) have gained much interest for their special activities and applications in organic synthesis.[3] However, other sulfur-centered radicals such as pentafluorosulfanyl radicals ($F_5S^{\bullet}$),[4a] thiocyanato ($NCS^{\bullet}$),[4b] and trisulfur radical anion ($S_3^{\bullet-}$)[4c] gained less attention for their few applications in organic reactions.[4] $S_3^{\bullet-}$ can be easily formed by the reaction of elemental sulfur with KOH in DMF at room temperature.[5] Although $S_3^{\bullet-}$ species has been known for more than 40 years,[5] applications for the synthesis of organosulfur compounds have been very limited.[6] The development of new reactions involving $S_3^{\bullet-}$ and its further applications are still great challenges.

Sulfur reagents such as K_2S have been widely used in transition-metal catalyzed sulfur insertion reactions.[7] However, there are no reports utilizing K_2S to initiate aryl radicals or radical anions from aryl halides under transition-metal free conditions (Scheme 1). Herein, we report a K_2S initiated sulfur insertion reaction with enaminones to construct benzothiazine derivatives *via* formation of two C–S bonds and C–X bond cleavage under transition metal-free conditions. As such, the



Scheme 1 Approaches for aryl sulfide.

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present reaction enables the synthesis of the benzothiazine derivatives under mild conditions and also attracts more attention for trisulfur radical anion ($S_3^{\bullet-}$) involved reactions under transition metal-free conditions.

Initially, the model reaction of 3-((2-iodophenyl)amino)-5,5-dimethylcyclohex-2-enone **1a** and K_2S **2a** was performed in DMF at 110 °C for 12 h catalyzed by 10 mol% CuI in the presence of 20 mol% of I_2 under Ar atmosphere. The [5 + 1] cyclization product 4*H*-benzo[*b*][1,4]thiazine derivative **3a** was obtained in 65% liquid chromatography yield (LC-yield). The structure of **3a** was confirmed by NMR, IR, HRMS and X-ray analysis (Fig. 2).

We further screened the reaction conditions and found that the reaction also proceeded even without the copper salt and iodine (for details see ESI†). Then different solvents such as CH_3CN, 1,4-dioxene, 1,2-dichloroethane (DCE), toluene, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF) and H_2O were tested for the reaction of **1a** and **2a** at 130 °C for 12 h under Ar atmosphere. As shown in Fig. 3, CH_3CN, 1,4-dioxene could give moderate yields of **3a**. Trace product **3a** could be detected when the reaction was carried out in DCE, toluene, THF and H_2O, respectively. Gratifyingly, the LC-yield of **3a** was dramatically increased to 75% by using DMSO as solvent. It should be noted that the reaction proceeded smoothly to give **3a** in 90% LC-yield when DMF was used.

Then other sulfur reagents such as cyclo-S_8, $Na_2S\cdot 9H_2O$, $NaHS\cdot H_2O$, $Na_2S_2O_3$ were applied in this reaction under transition metal-free conditions (Table 1). The reaction of **1a** with $Na_2S\cdot 9H_2O$ occurred smoothly to give **3a** in 80% LC-yield. $NaHS\cdot H_2O$ also showed a moderate activation with **1a** in this reaction to give **3a** 60% LC-yield. **3a** could also be obtained in 27% LC-yield when the sulfur was used. Only trace amount of **3a** was detected when **1a** reacted with $Na_2S_2O_3$ under the identical conditions.

To explore the potential applications of this method, a variety of enaminones **1** were examined (Table 2). Electron-donating substituents on the phenyl ring of enaminone such as –Me, –OMe, promoted the cross-coupling product **3b** and **3c** in excellent yield (95, 88%). The substitution pattern of the chlorine group made some difference to the reaction outcome (**3d**, **3e** and **3f**). The reaction of 3-(4-fluorophenylamino)-5,5-dimethylcyclohex-2-enone **1g** with **2a** also led to the desired product **3g** in 85% yield. Electron-withdrawing groups, such as NO_2, CF_3, also worked well and the desired products (**3h**, **3i**) were isolated in excellent yields, too. The reactions of other substituted enaminones **1i–l** with **2a** furnished the products **3i–l**

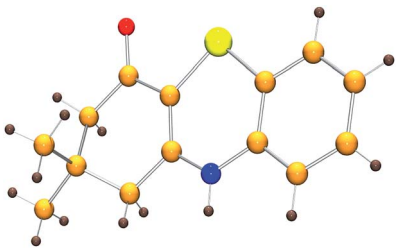


Fig. 2 Crystal structure of **3a**.

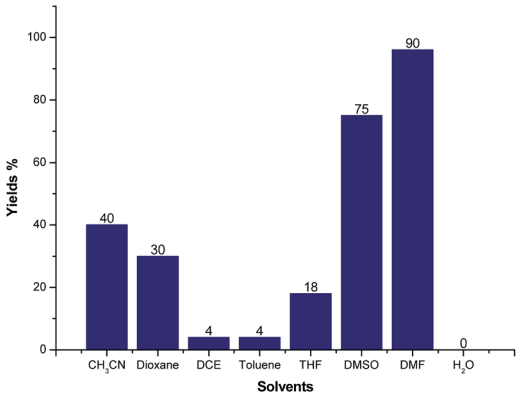
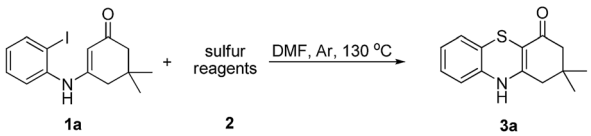


Fig. 3 The effect of different solvents. *Reaction conditions*: **1a** (0.5 mmol), **2a** (0.6 mmol), solvent (3 mL) at 130 °C, 12 h under Ar atmosphere. The yields were determined by LC analysis using biphenyl as the internal standard.

in moderate to excellent yields (47–96%). Unfortunately, when the unstable enaminone (*E*)-4-(phenylamino)pent-3-en-2-one **1n** was applied to the reaction, trace product **3n** could be detected.

Subsequently, enaminones 3-((2-chlorophenyl)amino)-6,6-dimethylcyclohex-2-enone **1a-Cl** and 3-((2-bromophenyl)-amino)-6,6-dimethylcyclohex-2-enone **1a-Br** instead of **1a-I** were applied to reaction with **2a**. The results indicated that chloro-functionalized enaminone **1a-Cl** showed poor reactivity but bromo-functionalized enaminone **1a-Br** showed competitive reactivity compared to iodo-functionalized enaminone **1a-I** and resulted in **3a** in 94% yield (Scheme 2). Some other bromo-functionalized enaminones reacted with **2a** also has been investigated (Table 3). The reactions of 3-((2,5-dibromophenyl)-amino)-5,5-dimethylcyclohex-2-enone and 3-((2,6-dibromophenyl)amino)-5,5-dimethylcyclohex-2-enone with K_2S were explored, and the desired products **3o** and **3p** were observed in 80% and 68% yields, respectively, leaving one bromide and another bromide substituents untouched. However, the reaction of 5,5-dimethyl-3-((2,4,6-tribromophenyl)amino)cyclohex-2-enone failed to isolate the corresponding product **3q**. The

Table 1 Yields of **3a** from **1a** for various sulfur reagents[a]



Reagent	Yield (%)
K_2S	80
Cyclo-S_8	27
$Na_2S\cdot 9H_2O$	80
$NaHS\cdot H_2O$	60
$Na_2S_2O_3$	Trace

[a] *Reaction conditions*: **1a** (0.5 mmol), **2** (0.6 mmol), DMF (3 mL) at 130 °C, 12 h under Ar atmosphere.

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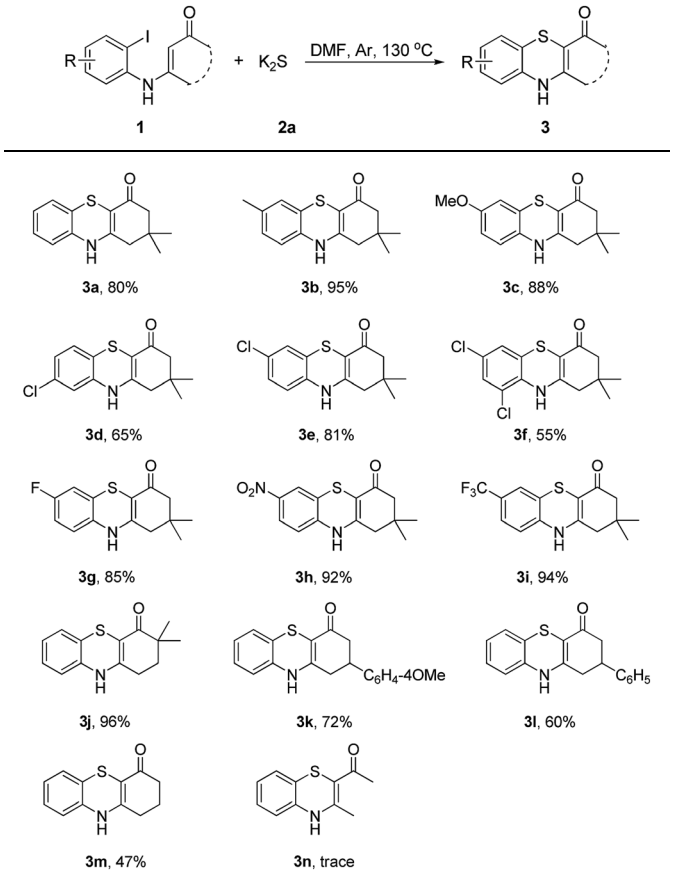
Table 2 Synthesis of 4*H*-benzo[*b*][1,4]thiazine derivatives[a]



[a] *Reaction conditions*: **1** (0.5 mmol), **2a** (0.6 mmol), DMF (3 mL) at 130 °C, 12 h under Ar atmosphere.

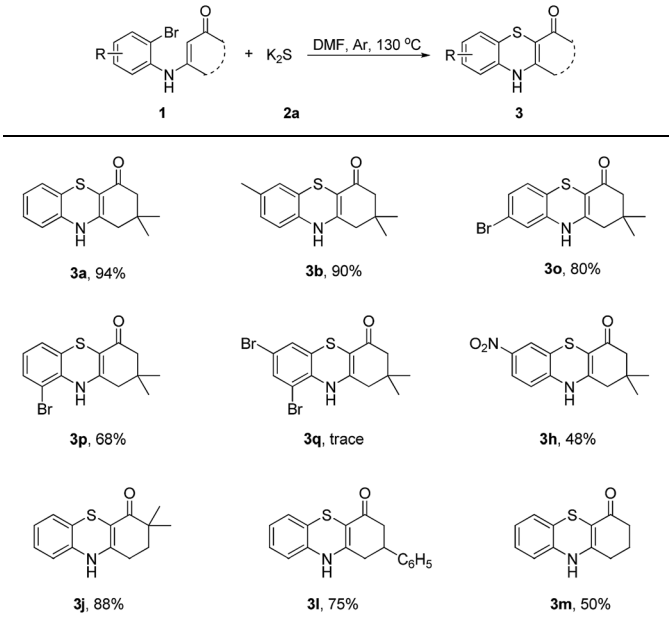
Scheme 2 The reaction with **2a**.

3-(2-iodo-4-nitrophenylamino)-5,5-dimethylcyclohex-2-enone **1h-Br** promoted the cross-coupling product **3h** in 48% yield. Other substituted enaminones (**1j-Br** to **1m-Br**) reacted with **2a** also furnished the desired products **3j-m** in moderate yields (50% to 88%).

Then, an attempt was made to achieve the efficient synthesis of 2-phenyl-4*H*-thiochromen-4-one derivatives with 2′-bromochalcones **4** as the starting materials (Table 4). The reaction of 2′-bromochalcone **4a** progressed well and gave the corresponding product **5a** in 51% yield. The 2′-bromochalcones with methyl, chloro and fluoro substituents, which could be useful for further derivatization, were found to be suitable for this reaction (**5b–d**). Besides aryl groups, substrates with thienyl group **4e** was also found to be appropriate for this reaction, and the corresponding product **5e** was obtained in 60% yield.

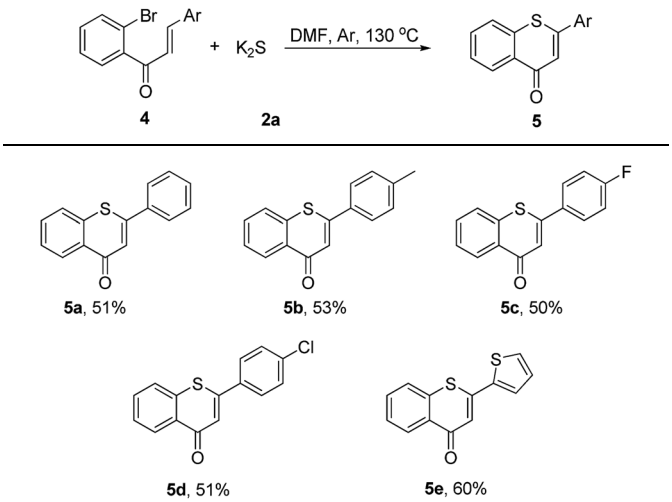
To explore the plausible mechanism of this reaction, we first analyzed K_2S using inductively coupled plasma atomic absorption spectroscopy (ICP-AAS). Indeed, 2–10 ppm of Cu, Pd, Fe species were detected in K_2S although its purity is >99.99%. It was found that adding 1000 times amounts of these metal salts

Table 3 Synthesis of 4*H*-benzo[*b*][1,4]thiazine derivatives[a]



[a] *Reaction conditions*: **1** (0.5 mmol), **2a** (0.6 mmol), DMF (3 mL) at 130 °C, 12 h under Ar atmosphere.

Table 4 Synthesis of 2-aryl-4*H*-thiochromen-4-one derivatives[a]



[a] *Reaction conditions*: **4** (0.5 mmol), **2a** (0.6 mmol), DMF (3 mL) at 130 °C, 12 h under Ar atmosphere.

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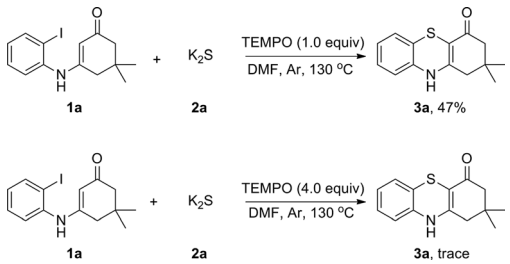
to the reaction system did not obviously enhance the reaction rate, which indicated that this reaction was not transition-metal catalyzed and the radical addition pathway was an apparent consideration to the mechanism. Therefore, radical-trapping experiments were performed as shown in Scheme 3. When 1.0 equiv. of TEMPO was added to the reaction the yield of **3a** was reduced to 47%. As the amount of TEMPO was increased to 4.0 equiv., the reaction was almost fully suppressed. This observation indicated that a radical pathway might be involved in the reaction.

To gain some insight into the interaction between K_2S and DMF or other solvents, an electron paramagnetic resonance (EPR) experiment was carried out (Fig. 4). A strong single EPR signal was observed in DMF solution of K_2S at room temperature (deep blue line). When the solvent was changed to DMSO, the EPR signal was significantly attenuated (purple line). As for the other solvents, almost no EPR signal was observed. Lelieur found similar EPR signals in liquid ammonia solution of sulfur, and identified it as the trisulfur radical anion ($S_3^{\bullet-}$).[8] Gratifyingly, our EPR parameter ($g = 2.02$) is very similar with the reported one detected by the DMF solution of $Na_2S\cdot 9H_2O$ and elemental sulfur at room temperature.[6b] So we suspected that a free radical $S_3^{\bullet-}$ might be generated from the solution of K_2S in DMF.

We further confirmed the presence of trisulfur radical anion ($S_3^{\bullet-}$) by the UV-visible spectra and Raman spectra studies (Fig. 5). From the UV-visible spectra, we could detect a characteristic absorption peak at about 550–700 nm wavelength in the DMF solutions of K_2S or $Na_2S\cdot 9H_2O$ and elemental sulfur. In addition, the Raman spectra results also gave us some strong evidence of the trisulfur radical anion ($S_3^{\bullet-}$).[9] The 531 cm^{-1} peak (ν_1) corresponds to the symmetric S–S stretching. The resonance phenomenon is induced *via* the absorption of $S_3^{\bullet-}$ by the laser radiation, which results in the high-order overtones ($2\nu_1 \approx 1068$ cm^{-1}, $3\nu_1 \approx 1597$ cm^{-1}, $4\nu_1 \approx 2124$ cm^{-1}) for the enhancement effects.[10]

We also found that the reaction takes place to give similar results under an argon atmosphere or in air. This observation indicated that DMF might be the oxidant for this reaction instead of oxygen or other oxidants. In order to prove this proposal, we tried the reaction of **1a** with **2a** in d^7-DMF (Fig. 6). From the crude ^1H NMR spectrum of this reaction, it was found that d^7-DMF was reduced to give **G′** (for further details see ESI†). This result indicates that $S_3^{\bullet-}$ was formed *via* the oxidation of S^{2-} by DMF, which is different with the one in Lei's work ($S_3^{\bullet-}$ was obtained by the disproportionation reaction of sulfur with $Na_2S\cdot 9H_2O$).[6b]



Scheme 3 Radical-trapping experiments.

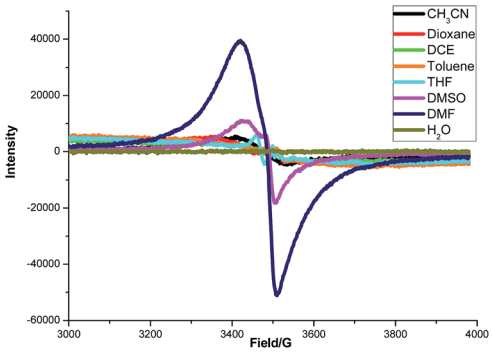


Fig. 4 EPR spectra of solutions of K_2S (0.6 mmol) in various solvents (3 mL) at 298 K.

Based on the reported literatures and above results, a $S_{RN}1$ type electron catalysis mechanism[11] is proposed in Scheme 4. DMF activates the electron-donating agent K_2S to give $S_3^{\bullet-}$ radical anion, radical anion **A** and electrons. An aryl halide radical anion **B** is generated from enaminone **1a** by single electron transfer (SET).[12] The elimination of I^- leads to an aryl radical **C** (the protonated species could be detected by LC-MS[13]), the radical **C** reacts with $S_3^{\bullet-}$ to form the intermediate **D**. The homolysis of intermediate **D** gives $S_2^{\bullet-}$ and a thiyl radical **E**, which subsequently undergoes intramolecular radical addition to afford the radical **F**. We propose that there are two possible pathways for the oxidation of $S_2^{\bullet-}$ to give $S_3^{\bullet-}$. One possibility is

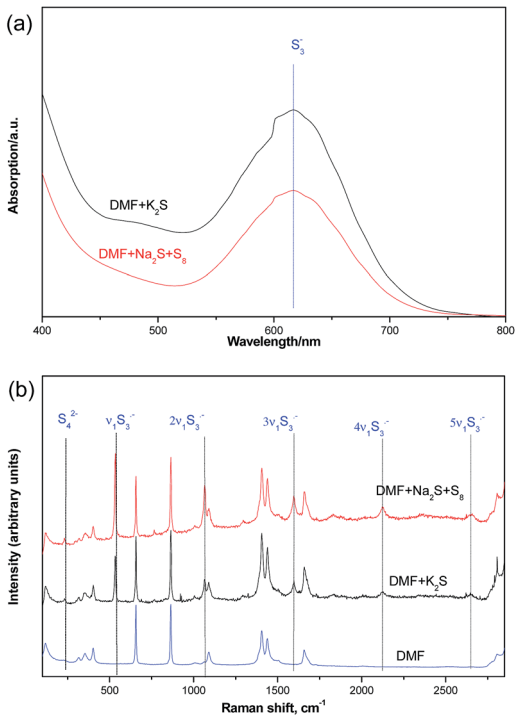


Fig. 5 UV-visible spectra (a) and Raman spectra (b) (632.8 nm) studies of interaction between K_2S and DMF.

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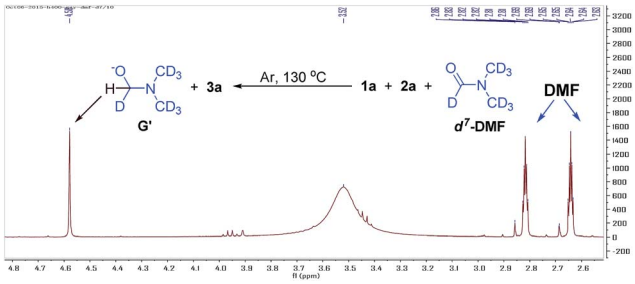
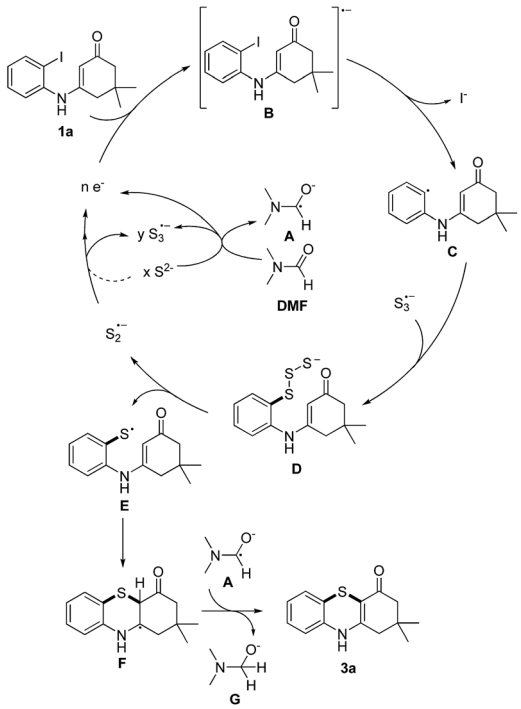


Fig. 6 ^{1}H NMR spectrum of the reaction of **1a** with **2a** in d^7-DMF.



Scheme 4 Plausible mechanism.

that $S_2^{\bullet-}$ dimerizes to afford the dianion S_4^{2-}, which then disproportionates to give blue $S_3^{\bullet-}$.[14] The other possibility is that $S_2^{\bullet-}$ reacts with S^{2-} to afford $S_3^{\bullet-}$ and the electrons. Following the electron transfer of **F** with **A**, anion **G** and **3a** are formed.

In summary, we have developed a K_2S initiated and electron-catalyzed sulfur insertion reaction with enaminones to construct the [5 + 1] cyclization product 4*H*-benzo[*b*][1,4]thiazine and 2-aryl-4*H*-thiochromen-4-one derivatives. This protocol provides a new, environment-friendly and simple strategy to the synthesis of the 4*H*-benzo[*b*][1,4]thiazine and 2-aryl-4*H*-thiochromen-4-one derivatives under transition metal-free, additive-free and oxidant-free conditions. The presence of the trisulfur radical anion was proven by EPR spectroscopy, and reasonable mechanisms have been proposed. Further investigations of the trisulfur radical anion triggered electron-catalyzed reactions under transition metal-free conditions are currently under study in our laboratory.

Acknowledgements

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13 The protonated species of radical intermediate **C** and the coupling intermediate of **C** with TEMPO were both detected by LC-MS.

14 S_4^{2-} can be detected from the solution of K_2S in DMF based on Raman spectra (Fig. 5, 234 cm^{-1} peak). According to this result and the literatures, we propose that $S_2^{\bullet-}$ might dimerise to afford the dianion S_4^{2-}, which then disproportionates to give blue $S_3^{\bullet-}$.(*a*) F. Gaillard, E. Levillain and J. P. Lelieur, *J. Electroanal. Chem.*, 1997, **432**, 129; (*b*) H.-L. Wu, L. A. Huff and A. A. Gewirth, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1709.

$$4\,S_2^{\bullet-} \longrightarrow 2\,S_4^{2-} \underset{2e^-}{\rightleftharpoons} 2S_4^{\bullet-} \longrightarrow S_8^{2-} \xrightarrow{S_4^{2-}} 2S_6^{2-} \longrightarrow 4\,S_3^{\bullet-}$$

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