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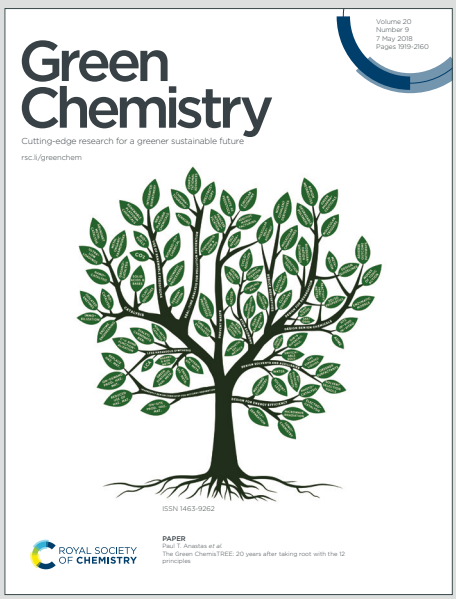

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Visible-Light-Promoted Cascade Cyclization towards Benzo[*d*]imidazo[5,1-*b*]thiazoles under Metal- and Photocatalyst-Free Conditions

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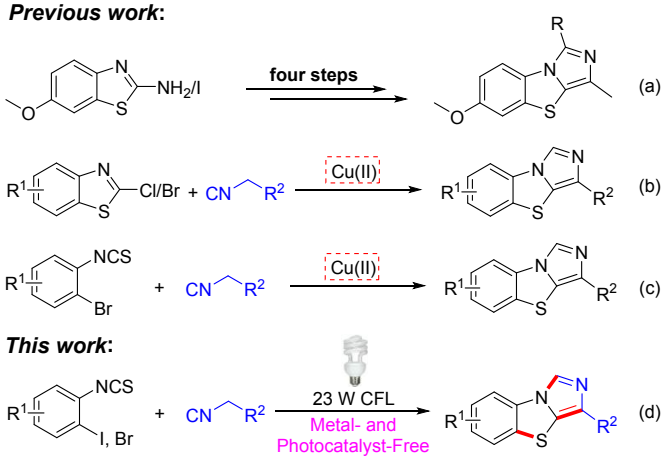
The visible-light-promoted cascade cyclization of 2-haloaryl isothiocyanates and isocyanides to access benzo[*d*]imidazo[5,1-*b*]thiazoles has been realized efficiently under metal- and photocatalyst-free conditions. The reaction mechanism was explored by several preliminary experiments involving reactive intermediate, free radical inhibitors, and corresponding photoelectric spectra. This protocol possesses some advantages over the previous methods such as readily available and inexpensive substrates, metal catalyst needlessness, step and atom economy, and mild reaction conditions.

Introduction

Heterocycles are diverse and abundant, accounting for more than half of current reported organic compounds.[1] In addition, many heterocyclic compounds possess excellent pharmaceutical, biological and photoelectric properties.[2] Among them, thiazole[3] and imidazole[4] are two significant types of heterocyclic skeletons, which widely present in a variety of common clinical drugs.[5-6] In particular, as a combination of the above two heterocyclic structures, imidazothiazoles are important heterocyclic compounds exhibiting a wide range of physiological activities.[7] Although several methods of construction imidazo[2,1-*b*]thiazoles[8] have been developed, the synthetic strategies of functionalized imidazo[5,1-*b*]thiazoles[9] are very limited and contain certain disadvantages. In 2013, Gharat and co-workers developed a route to prepare benzo[*d*]imidazo[5,1-*b*]thiazoles from substituted benzothiazoles (Scheme 1a).[7a] However, this conversion may generally require four steps to complete. In 2015, the team of Zhu reported a cycloaddition of 2-halogenated benzothiazoles and isocyanides to access four benzo[*d*]imidazo[5,1-*b*]thiazole derivatives with the help of a copper catalyst (Scheme 1b).[9a] Subsequently, our research group[9b] and Hao *et al.*[9c] realized and reported the copper-catalyzed cascade reactions of 2-haloaryl isothiocyanates and isocyanides to construct benzo[*d*]imidazo[5,1-*b*]thiazole compounds, respectively (Scheme 1c). Although the above



Scheme 1 Synthesis of benzo[*d*]imidazo[5,1-*b*]thiazoles

one-pot methods to obtain benzo[*d*]imidazo[5,1-*b*]thiazoles have higher efficiency, copper catalysts are necessary. Under these circumstances, the residues of trace amounts of copper catalysts in benzo[*d*]imidazo[5,1-*b*]thiazoles are usually inevitable. Therefore, it is meaningful to develop green, efficient, mild, and high atom economy synthetic methods of benzo[*d*]imidazo[5,1-*b*]thiazole derivatives.

Visible light is a non-toxic, renewable, and abundant energy source. Therefore, reactions assisted by visible light are more in line with the requirements of expanding some green, sustainable and environmentally harmonious synthesis strategies.[10] Up to now, homogeneous photocatalysts mainly including organic dyes and complexes of ruthenium or iridium have been employed in photocatalytic reactions.[11] In addition, several kinds of heterogeneous photocatalysts,[12] such as titanium dioxide (TiO_2),[13] polymeric graphitic carbon nitrides (CN),[14] magnetic photocatalytic materials,[15] metal–organic

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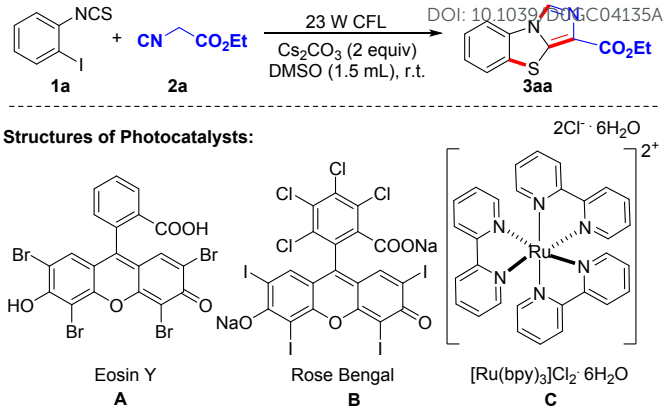
frameworks (MOFs),[16] and covalent organic frameworks (COFs),[17] have also been successfully developed and used to assist photocatalytic conversions. Although many cheap and easily recyclable photocatalysts are mentioned in these photocatalytic works, the use of photocatalysts inevitably increases the cost and the complexity of reaction systems. In comparison, the development of reactions involving photoactive substrates without using any additional photosensitive catalysts can solve the problems of cost and complexity of reaction systems to a certain extent. Based on our continuous efforts in proposing the preparation methods of benzo[*d*]imidazo[5,1-*b*]thiazoles and other heterocyclic compounds,[9b,18] we herein report a visible-light-promoted tandem conversion of 2-haloaryl isothiocyanates and isocyanides to access benzo[*d*]imidazo[5,1-*b*]thiazoles without the need of any metal and photocatalyst (Scheme 1d). Compared with the previous strategies, this program possess some highlights such as readily available and inexpensive substrates, metal catalyst needlessness, step and atom economy, and mild reaction conditions.

Results and discussion

At the beginning, 1-iodo-2-isothiocyanatobenzene (**1a**) (0.2 mmol, 1.0 equiv) was introduced to react with ethyl 2-isocyanoacetate (**2a**) (0.3 mmol, 1.5 equiv) assisted by Cs_2CO_3 (2 equiv) at room temperature under the irradiation of a 23 W compact fluorescent light (CFL) for 15 h under air. The product of ethyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (**3aa**) was achieved with a yield of 78% (Table 1, entry 1). Reactions involved other bases such as K_2CO_3, CsOAc, DBU (2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine) or no base was employed, generating **3aa** in 9−71% yields (entries 2−5). In order to eliminate the metal catalytic process caused by the residual metal in the base, $CsCO_3$ with a purity of 99.995% was employed, showing **3aa** a yield of 79% (entries 6). The results of solvents tests indicated that DMSO is more efficient than other solvents for this reaction (entries 1, 7−9). Moreover, when the light source was changed to 12W blue LED, the yield of **3aa** was reduced to 66% (entries 10). Also, no **3aa** was generated without the irradiation (entries 11). Besides, three common photocatalysts did not promote the conversion (entries 12−14).

The scope and generality of 2-haloaryl isothiocyanates and isocyanides were investigated in turn under the above optimized conditions (Table 2). It was found that when **2a** was treated with 1-iodo-2-isothiocyanatobenzene or 1-bromo-2-isothiocyanatobenzene under standard conditions, the yields of product **3aa** were 78% and 41%, respectively. In contrast, the transformation involving 1-chloro-2-isothiocyanatobenzene could not yield any benzo[*d*]imidazo[5,1-*b*]thiazoles. Given good reactivity of 1-iodo-2-isothiocyanatobenzene, the subsequent reactions employed 2-iodoaryl isothiocyanates as the substrates. When various 2-iodoaryl isothiocyanates carrying a electron-donating substituent such as methyl, *tert*-butyl and methoxy at different phenyl positions were treated with 2-isocyanoacetate (**2a**),

Table 1 Optimization studies[a]



Entry	Variations	Yield (%)[b]
1	**none**	**78**
2	K_2CO_3 instead of Cs_2CO_3	71
3	CsOAc instead of Cs_2CO_3	42
4	DBU instead of Cs_2CO_3	14
5	without Cs_2CO_3	9
6	99.995% pure Cs_2CO_3	79
7	DMF instead of DMSO	35
8	CH_3CN instead of DMSO	0
9	1,4-dioxane instead of DMSO	13
10	12 W blue LED	66
11	without light	0
12	1 mol% of **A** was used as photoredox catalyst	77
13	1 mol% of **B** was used as photoredox catalyst	74
14	1 mol% of **C** was used as photoredox catalyst	68

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), base (2 equiv), solvent (1.5 mL), temperature (rt, ~25 °C), time (15 h), under air. [b] Isolated yields.

72−73% yields of benzo[*d*]imidazo[5,1-*b*]thiazoles (**3ba**−**3fa**) were achieved. Also, the reactions involving 2-iodoaryl isothiocyanates with electron-withdrawing substituents such as fluorine, chlorine, bromine, and nitro proceeded smoothly, providing products **3ga**−**3le** in 48−72% yields. To our satisfaction, the transformation involving heterocyclic isothiocyanate of 2-iodo-3-isothiocyanatopyridine (**1m**) also gave the product ethyl imidazo[5',1':2,3]thiazolo[5,4-*b*]pyridine-8-carboxylate (**3ma**) with a yield of 76%. Moreover, several isocyanides with different carboxylate substituents were tested, and the corresponding products (**3ab**−**3ah**) were achieved in 70−84% yields. In addition, the cascade cyclization reactions of 1-((isocyanomethyl)sulfonyl)-4-methylbenzene (**2i**) or 2-isocyanoacetic acid (**2j**) with **1a** provided products 3-

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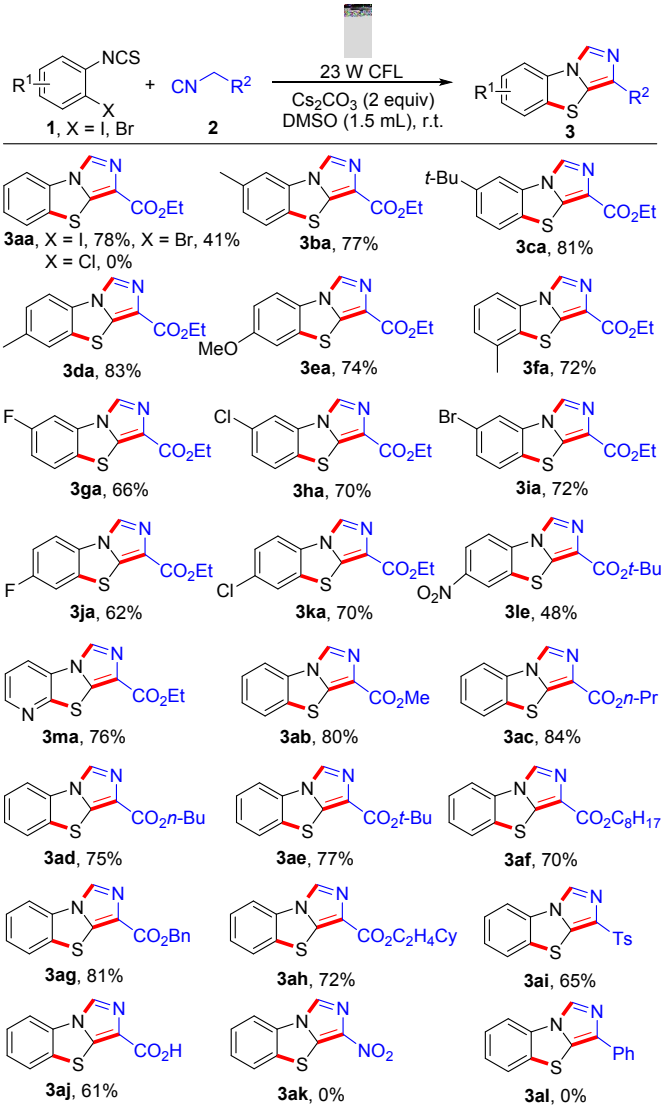
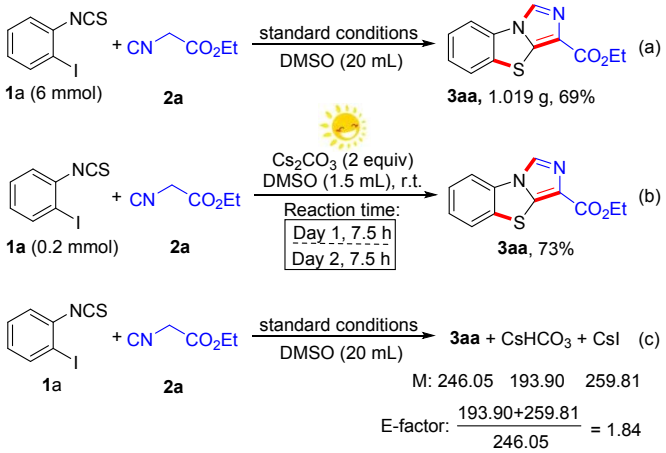
tosylbenzo[*d*]imidazo[5,1-*b*]thiazole (**3ai**) or benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylic acid (**3aj**) in 61–65% yields. However, nitro and phenyl substituted isonitrile substrates failed to give any products of benzo[*d*]imidazo[5,1-*b*]thiazoles.

Table 2 Substrate scope[a]



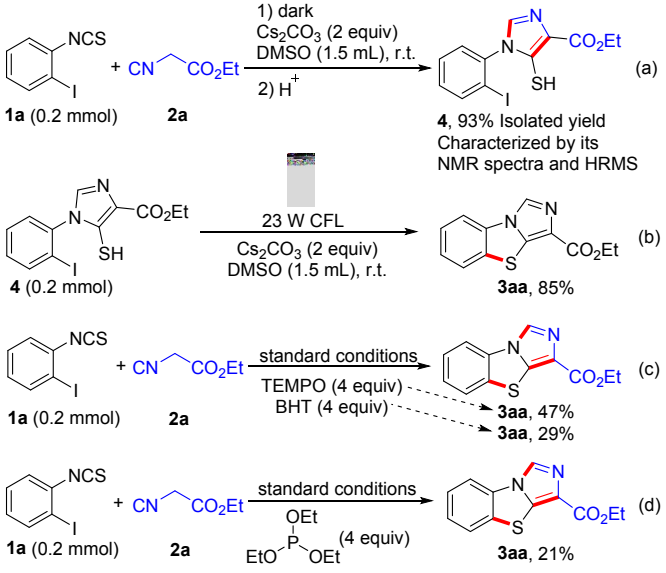
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), Cs_2CO_3 (2 equiv), DMSO (1.5 mL), rt, 15 h, under air, isolated yield.

Next, the gram-scale preparation experiment was carried out under the standard conditions with 6 mmol of **1a**, and the product **3aa** was successfully given in 69% yield (1.019 g) (Scheme 2a). Interestingly, when the conversion could be run for 15 h under natural light irradiation (two days, 7.5 hours per day), the target compound **3aa** was obtained in 73% yield (Scheme 2b). Accordingly, the data of two experiments prove the possibility of this protocol in the large-scale preparation of benzo[*d*]imidazo[5,1-*b*]thiazoles and the utilize of natural light. In addition, the E-factor was calculated to be 1.84 to investigate the environmental impact of the formation of benzo[*d*]imidazo[5,1-*b*]thiazoles in this transformation (Scheme 2c).



Scheme 2 Gram-scale preparation, natural light irradiation experiment and calculation of E-factor

The reaction mechanism was first explored by several experiments involving reactive intermediate and free radical inhibitors. It was discovered that when **1a** reacted with **2a** under dark conditions for 15 h and then acidified to pH = 5 with hydrochloric acid, intermediate ethyl 1-(2-iodophenyl)-5-mercapto-1*H*-imidazole-4-carboxylate (**4**) was obtained in 93% yield (Scheme 3a). **4** could be further transformed into product **3aa** with a yield of 85% under standard conditions (Scheme 3b). The series of operations illustrate that **4** may be the active intermediate for this transformation. Two common free radical inhibitors TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy) and BHT (butylated hydroxytoluene) were added into the reactions of **1a** and **2a**, respectively, resulting in the significantly reduced yields of **3aa** (Scheme 3c). In addition, an effective aryl radical scavenger triethoxyphosphorus[19] also strongly inhibited the formation of the product **3aa** (Scheme 3d). Although we did not detect any free radical capture products by HRMS, these results suggest that this transformation should involve a free radical step.



Scheme 3 The mechanism research experiments

To gain more insight into the C–S cross-coupling process, we performed UV–vis spectroscopic measurements on various combinations of **1a**, **2a**, **4**, and Cs_2CO_3 in DMSO at 1.5×10^{-3} M concentration for each species (Fig. 1a). A new peak (λmax = 330 nm) was observed when the cycloaddition intermediate **4** and Cs_2CO_3 were mixed. This peak is proposed to result from the absorption of an intramolecular electron donor–acceptor (EDA) complex[19] formed by the association of the thiolate anion and aryl iodide. The visible-light absorption of this EDA complex in DMSO at a higher concentration (0.05 M) extended to the 400–625 nm region (Fig. 1b). When testing the visible light absorption properties of this EDA complex in different solvents, the absorption value in DMSO was significantly better than other solvents (Fig. 1c). This is consistent with the experimental data obtained in the optimization table (Table1, entries 1, 7–9). In addition, we also studied the redox electrode potential of Intermediate **4** through cyclic voltammetry experiments. Two oxidation peaks (1.19, 1.44 vs Ag/AgCl) and two reduction peaks (-0.82, -1.57 vs Ag/AgCl) were found (Fig. 1d).

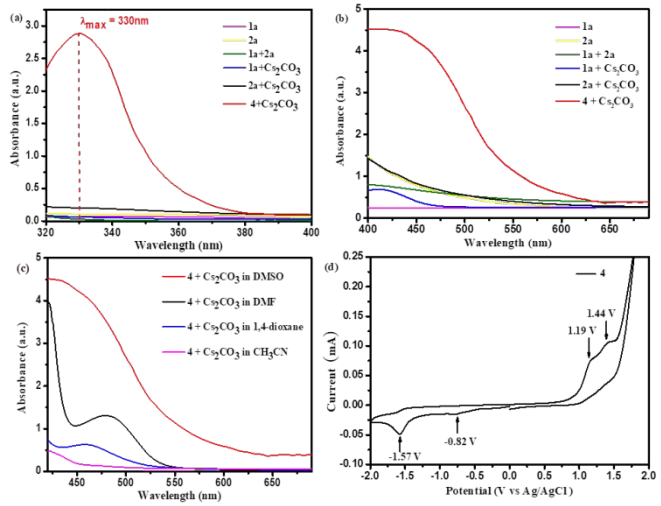


Fig. 1 (a, b) UV–vis absorption spectra of mixtures of **1a**, **2a**, **4**, and Cs_2CO_3 in DMSO at concentrations of (a) 1.5×10^{-3} M and (b) 0.05 M for each species. (c) Visible light absorption spectra of **4** and Cs_2CO_3 in different solvents. (d) Cyclic voltammetry experiments of **4**.

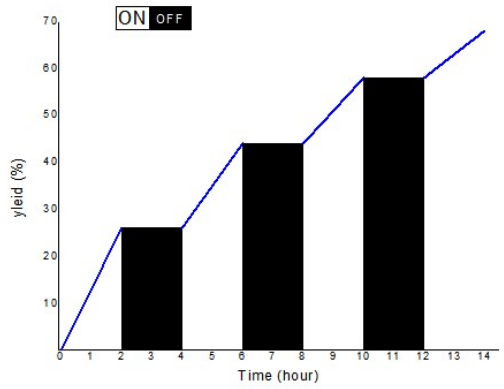
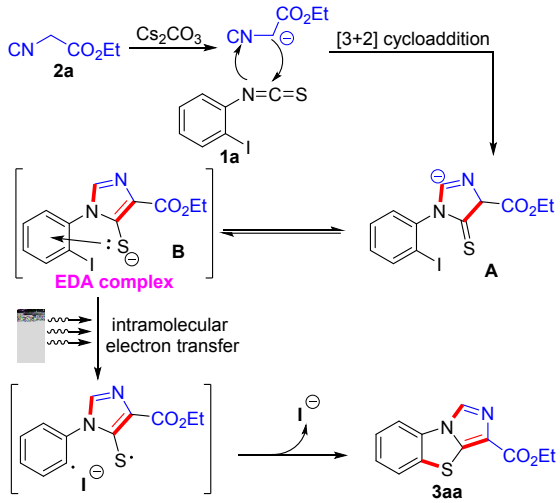


Fig. 2 Visible light irradiation ON/OFF experiment

In addition, a visible light irradiation ON/OFF experiment was performed, showing that the irradiation should be essential for the continuous progress of this transformation (Fig. 2).

Refer to the above exploration experiments and related reports,[20] a possible conversion path is thus presented (Scheme 4). Initially, **1a** and **2a** undergo a 3+2 cycloaddition reaction under the promotion of $CsCO_3$ to produce intermediate **A**, which may pass through the isomerization to yield the intermediate **B**. In intermediate **B**, the electron-rich thiolate anion and the electron-poor aryl iodine moiety are first associated to form an EDA complex. This EDA complex can be activated under light irradiation and undergo an intramolecular single electron transfer process to obtain an aryl radical, a sulfur radical and an iodine anion. Finally, the product **3aa** is obtained through the intramolecular free radical coupling reaction.



Scheme 4 Proposed mechanistic pathway

Conclusions

In conclusion, a mild, efficient and low toxicity synthesis strategy has been proposed for the preparation of diverse benzo[*d*]imidazo[5,1-*b*]thiazoles *via* the visible-light-promoted tandem cyclization of 2-haloaryl isothiocyanates and isocyanides. Of note, this conversion does not employ any metals or photocatalysts, and ultimately resulting in fewer by-products. It offers a green and sustainable way for the preparation of diverse useful benzo[*d*]imidazo[5,1-*b*]thiazole derivatives.

Author contributions

Kelu Yan: Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing; Min Liu: Conceptualization, Data curation, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing; Jiangwei Wen: Investigation, Methodology, Resources, Software, Supervision; Xiao Liu: Data curation, Formal Analysis,

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Investigation, Methodology, Software; Xinyue Wang: Formal Analysis, Investigation, Methodology, Validation; Xinyu Chen: Formal Analysis, Investigation, Methodology, Validation; Jing Li: Formal Analysis, Investigation, Methodology; Shao Wang: Formal Analysis, Investigation, Methodology; Xiu Wang: Formal Analysis, Resources, Software, Supervision; Hua Wang: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. All authors approve the current version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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