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Palladium-catalyzed asymmetric allenylic alkylation: construction of multiple chiral thiochromanone derivatives†

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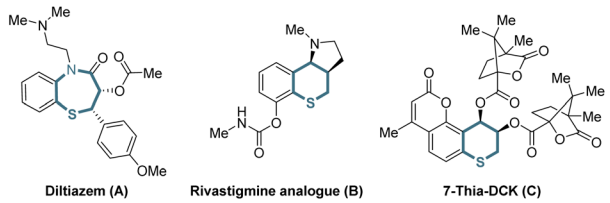
The development of a new strategy for the construction of chiral cyclic sulfide-containing multiple stereogenic centers is highly desirable. Herein, by the combination of base-promoted retro-sulfa-Michael addition and palladium-catalyzed asymmetric allenylic alkylation, the streamlined synthesis of chiral thiochromanones containing two central chiralities (including a quaternary stereogenic center) and an axial chirality (allene unit) was successfully realized with up to 98% yield, 49.0 : 1 dr and >99% ee.

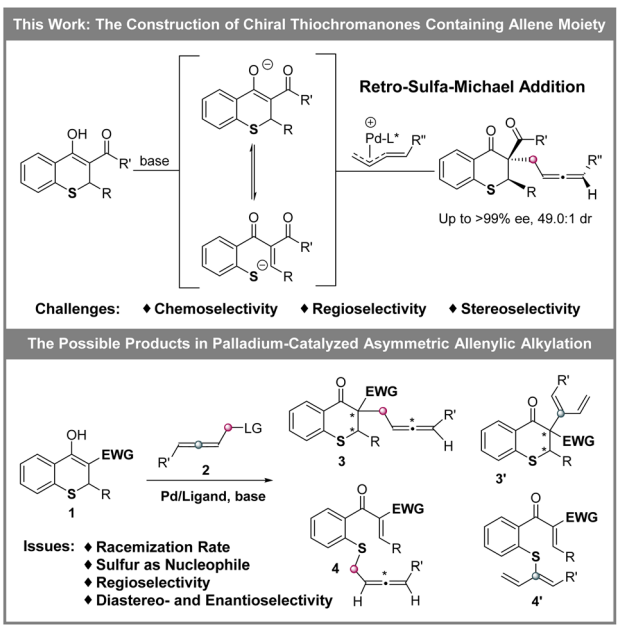
Introduction

Organic sulfur compounds play important roles in pharmaceuticals, natural products and other fields, in which molecules containing chiral cyclic sulfide skeletons generally have special biological activity.[1] For example, diltiazem (**A**),[2a] a calcium channel blocking agent, is used for treating supraventricular tachycardia, a rhythm disturbance of the heart. Additionally, the rivastigmine analogue (**B**)[2b] is synthesized as an acetylcholine-esterase (AChE) inhibitor for the treatment of Alzheimer's disease, and 7-thia-DCK (**C**)[2c] is an anti-AIDS agent (Scheme 1). Therefore, developing simple and efficient methods for the synthesis of chiral cyclic sulfide derivatives has become an intriguing area. Among the developed methods, organocatalytic sulfa-Michael-initiated cascade reactions are particularly appealing, which construct chiral cyclic sulfides containing one or more stereocenters.[3] In contrast, metal-catalyzed asymmetric reactions[4] are underexplored owing to the poisoning of metal catalysts by sulfur,[5] especially sulfur anions. Considering thiochromanes are important components of cyclic sulfide derivatives,[2b,c,6] it is vital to build chiral thiochromane derivatives containing multiple stereogenic centers.

The allene moiety is present widely in natural products and bioactive compounds,[7] and is an extremely versatile functional group in organic synthesis as well.[8] Recently, Pd-catalyzed asymmetric allenylic alkylations[9] have been developed as an efficient approach to construct chiral allenes. Previously, metal-catalyzed asymmetric reactions to build multiple chiral compounds, utilizing retro-oxa-Michael addition to simultaneously racemize two stereocenters, have been developed.[10] However, these asymmetric reactions involving a retro-sulfa-Michael addition process



Scheme 1 Selected bioactive cyclic sulfide derivatives.



Scheme 2 Construction of multiple chiral thiochromanone derivatives.

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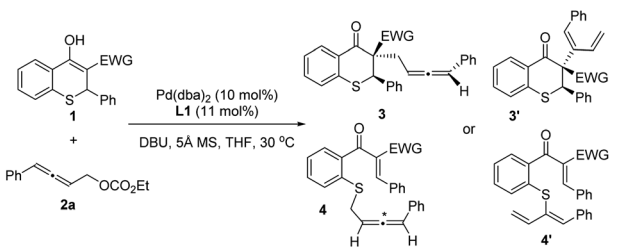
were less developed, in which only organocatalytic examples were reported.[3d,h,11] Combining palladium-catalyzed asymmetric allenylic alkylation and retro-sulfa-Michael addition to construct multiple chiral thiochromanone derivatives, some issues would need to be considered. (1) The rate of the racemization process *via* retro-sulfa-Michael addition should be faster than the rate of the next allenylic alkylation. (2) The sulfur is also nucleophilic,[12] which would compete with the carbon nucleophile, leading to different chemoselective products. (3) Regioselective products would be observed with an electrophilic π-allylpalladium intermediate (allene partner).[13] (4) The precise control of multiple chiralities including axial and central chirality is also a challenge. Hence, multiple possible products might be produced (Scheme 2). In this article, we reported the synthesis of enantioenriched multiple substituted thiochromanone derivatives containing two central chiralities and an axial chirality through the combination of retro-sulfa-Michael addition and palladium-catalyzed allenylic alkylation under basic conditions with up to 49.0 : 1 dr and >99% ee.

Results and discussion

The regio- and chemoselectivity of asymmetric allenylic alkylation might be ascribed to the electron-withdrawing group (EWG) in the thiochromanone derivatives. Thus, we initially explored the effect of electron-withdrawing groups on the reaction (Table 1). Just as we speculated, different electron-withdrawing groups led to regio- and chemoselective isomers on the allenylic alkylation. When the nitro group was used as the EWG, the chemoselective isomer **4aa** with sulfur as a nucleophile was observed (entry 1). Then, the desired product **3ba** with carbon as a nucleophile was obtained when the acetyl group was introduced as the EWG instead of the nitro group

Table 1 Effect of the electron-withdrawing group (EWG)[a]



Entry	EWG	Product	Yield[b] (%)	d*r*[b] (%)	ee[c] (%) Major	Minor
1	NO_2 (**1a**)	**4aa**	74	—	84	—
2	C(O)Me (**1b**)	**3ba**	94	3.5 : 1	70	90
3	CO_2Me (**1c**)	**3ca**	94	14.7 : 1	98	31
4	$C(O)N(CH_2)_5$ (**1d**)	**3da**	12	5.0 : 1	96	5
		4'da	84	—	—	—

[a] Reaction conditions: **1** (0.1 mmol), **2a** (1.5 equiv.), $Pd(dba)_2$ (10 mol%), **L1** (11 mol%), DBU (1.2 equiv.), THF (1.0 mL), 5 Å MS (50 mg), 30 °C, 10–24 h. [b] Yield and diastereomeric ratio were measured by analysis of ^1H NMR spectra using 1,3,5-trimethoxybenzene as the internal standard. [c] Determined by HPLC.

with low diastereoselectivity (entry 2). It is delightful that 14.7 : 1 dr was gained using the methoxycarbonyl as the EWG (entry 3).

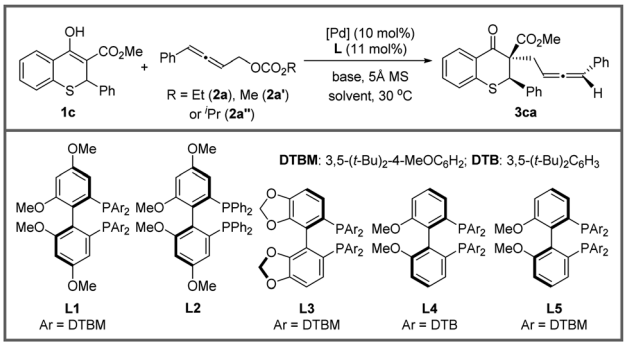
In addition, using amido as the EWG, the regio- and chemoselective isomer **4′da** was discovered as the main product when nucleophilic **1d** reacted with π-allylpalladium species. The yield of the desired product **3da** was only 12% with 5.0 : 1 dr and 96% ee for the major diastereoisomer (entry 4). Besides, using 1,3-bis(diphenylphosphino)propane as the ligand, trace *rac*-**3′da** was observed, in which different isomers might be obtained owing to the effect of ligand. On the whole, methoxycarbonyl should be the optimal electron-withdrawing group, with which the allenylic alkylation could proceed smoothly to deliver the desired major isomer.

Afterwards, the optimization of the asymmetric allenylic alkylation was examined using thiochromanone **1c** and allenylic carbonates **2** as substrates. First, different allenylic carbonates were screened (Table 2, entries 1–3) and ethyl (4-phenylbuta-2,3-dien-1-yl) carbonate **2a** might be better (entry 1). We next investigated the effect of solvent on this alkylation reaction (entries 4–6). The reactions performed smoothly in a variety of solvents, offering good stereoselectivities and reactivities. Then, tetrahydrofuran was chosen as the optimal solvent. Next, organic and inorganic bases were investigated, and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) still performed better (entries 7–9).

A chiral ligand, as we all know, is the key to stereoselectivity in the asymmetric reaction. Different axially chiral bisphosphine ligands with large steric hindrance were screened in the asymmetric allenylic alkylation (entries 11–13), and the large steric hindrance was necessary (entries 1 and 10). Surprisingly, the reaction delivered the desired product in 18.6 : 1 dr with **L4**. Subsequently, different catalyst precursors were examined with **L4**, including $Pd_2(dba)_3$, $[Pd(C_3H_5)Cl]_2$ and $Pd(OAc)_2$, with which all reactions resulted in lower diastereoselectivities (entries 14–16). Lastly, to further improve the diastereoselectivity and enantioselectivity, the effect of temperature was tested (entries 17–18). When the temperature decreased, higher stereoselectivity could be achieved under −20 °C. Finally, optimized conditions were established in entry 18 of Table 2.

Under the optimized reaction conditions, thiochromanone derivatives **1b–1p** were reacted with **2a** to explore the generality of the substrates (Scheme 3). Fortunately, thiochromanone derivatives with various aryl substituted R^1 could react smoothly in this palladium-catalyzed asymmetric allenylic alkylation to furnish the desirable products in good yields (82–96%), diastereoselectivities (24.0:1–49.0 : 1) and enantioselectivities (98–99%), which displayed valuable functional group tolerance in aromatic rings including methyl, fluoro, chloro, bromo and methoxyl. Among them, the substrate with an electron-rich substituent is relatively more active than that with an electron-deficient substituent (for details about reaction time, please see the ESI†). The reaction was slightly sensitive to the steric bulk of R^1. When *o*-tolyl (**1e**) was introduced, the reactivity, diastereoselectivity and enantioselectivity of this alkylation were a little lower. Notably, the halogens in the *para*-position of the aromatic ring (**1h–1j**) could slimly improve the

Table 2 Condition optimization[a]

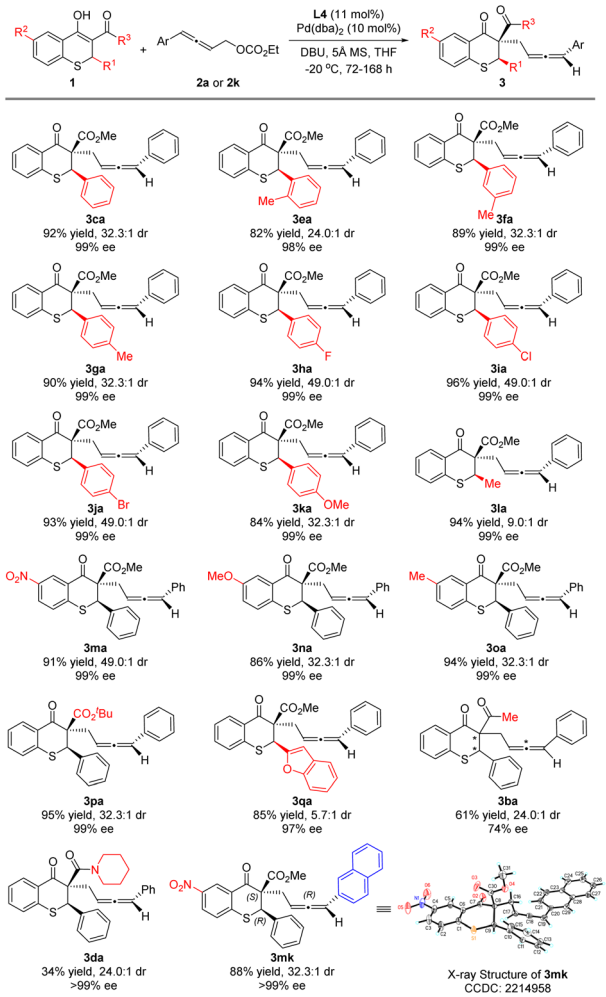


Entry	Solvent	Base/**L**	[Pd]	Yield[b] (%)	dr[b]	ee[c] (%) Major/minor
1	THF	DBU/**L1**	$Pd(dba)_2$	94	14.7 : 1	98/31
2[d]	THF	DBU/**L1**	$Pd(dba)_2$	>95	12.7 : 1	97/59
3[e]	THF	DBU/**L1**	$Pd(dba)_2$	>95	12.7 : 1	97/30
4	MeCN	DBU/**L1**	$Pd(dba)_2$	91	14.2 : 1	98/42
5	DMF	DBU/**L1**	$Pd(dba)_2$	90	14.0 : 1	97/11
6	Toluene	DBU/**L1**	$Pd(dba)_2$	>95	11.4 : 1	96/69
7	THF	Et_3N/**L1**	$Pd(dba)_2$	92	5.1 : 1	90/83
8	THF	TMG/**L1**	$Pd(dba)_2$	>95	8.7 : 1	95/84
9	THF	KO^{t}Bu/**L1**	$Pd(dba)_2$	>95	11.0 : 1	97/55
10	THF	DBU/**L2**	$Pd(dba)_2$	>95	4.0 : 1	79/31
11	THF	DBU/**L3**	$Pd(dba)_2$	>95	9.8 : 1	98/77
12	THF	DBU/**L4**	$Pd(dba)_2$	>95	18.6 : 1	95/30
13	THF	DBU/**L5**	$Pd(dba)_2$	>95	15.0 : 1	98/65
14	THF	DBU/**L4**	$Pd_2(dba)_3$	>95	15.3 : 1	98/54
15	THF	DBU/**L4**	$[Pd(C_3H_5)Cl]_2$	86	13.3 : 1	98/16
16	THF	DBU/**L4**	$Pd(OAc)_2$	>95	15.0 : 1	98/9
17[f]	THF	DBU/**L4**	$Pd(dba)_2$	>95	31.0 : 1	98/11
18[g]	THF	DBU/**L4**	$Pd(dba)_2$	92[h]	32.3 : 1	99/52

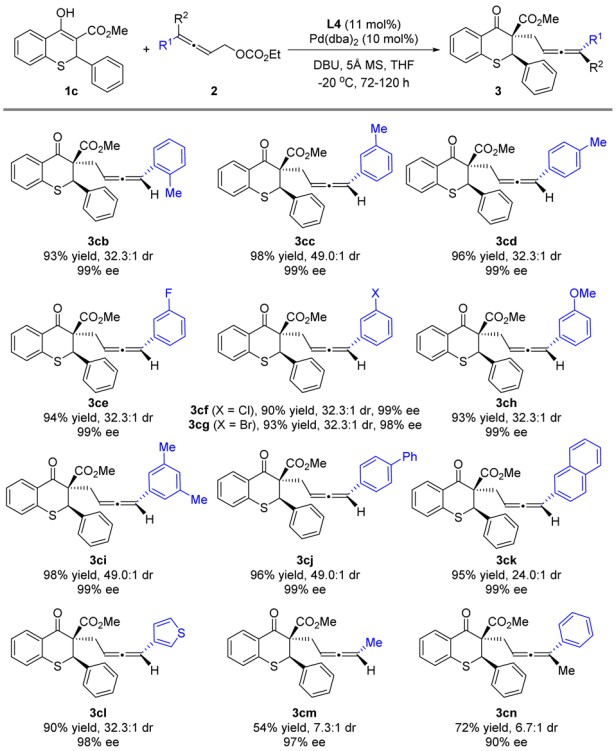
[a] Reaction conditions: **1c** (0.1 mmol), **2a** (1.5 equiv.), [Pd] (10 mol%), **L** (11 mol%), base (1.2 equiv.), solvent (1.0 mL), 5 Å MS (50 mg), 30 °C, 10–72 h. [b] Yield and diastereomeric ratio were measured by analysis of ^{1}H NMR spectra using 1,3,5-trimethoxybenzene as the internal standard. [c] Determined by chiral HPLC. [d] **2a′** instead of **2a**. [e] **2a″** instead of **2a**. [f] 0 °C instead of 30 °C. [g] −20 °C instead of 30 °C. [h] Isolated yield for the reaction at the 0.2 mmol scale, 72 h.

diastereoselectivity to 49.0 : 1. However, alkyl (methyl) had a negative effect on the diastereoselectivity (**1l**), which was 9.0 : 1. Furthermore, various R^2 groups were well tolerated, such as the strong electron-withdrawing nitro group (**1m**), electron-donating methoxy group (**1n**) and methyl group (**1o**). Increasing the steric hindrance of the R^3 group from methoxyl to *tert*-butoxyl, the reaction delivered the desired product **3pa** in 95% yield, 32.3 : 1 dr and 99% ee for the major diastereoisomer. We also investigated the thiochromanone derivative bearing the heterocyclic aromatic substituted group (2-benzofuranyl) and found that it gave the corresponding product **3qa** in 85% yield, albeit in lower diastereoselectivity (5.7 : 1 dr) and 97% ee for the major diastereoisomer. When **1b** with acetyl instead of methoxycarbonyl reacted with **2a**, the strong impact of ligands was observed after screening a series of chiral ligands, and (1*R*,1′*R*,2*S*,2′*S*)-DuanPhos was selected as the optimal ligand, with which the reaction delivered **3ba** at 30 °C in 61% yield, 24.0 : 1 dr and 74% ee for the major diastereoisomer. When the reaction temperature was decreased to 0 °C, the reaction could not perform. Besides, thiochromanone **1d** with the amide group reacted with **2a** under the optimized conditions to deliver the desired product **3da** with low 34% yield, in which there was the side product **4′da** with 48% yield and a little recovered **1d**. To assign the absolute configuration, **3mk** was synthesized and its absolute configuration was assigned as (2*R*,3*S*,R_a) by X-ray diffraction analysis (for details, please see the ESI†).

Reactions of **1c** with various allenylic carbonates **2b–2m** were next investigated (Scheme 4). The methyl substituent at the *ortho*, *meta* or *para*-position on the benzene ring of the allenylic carbonates (**2b–2d**) almost did not affect the stereoselectivity of the reaction, and better diastereoselectivity was obtained with the *meta*-position substituent. Subsequently, when the fluoro, chloro, bromo or methoxy group was introduced at the *meta*-position, the alkylation reaction underwent smoothly to deliver **3ce**, **3cf**, **3cg** or **3ch** in satisfactory yield, excellent ee and dr. Similarly, the reaction was conducted with 3,5-dimethylphenyl



Scheme 3 Substrate scope for the thiochromanone derivatives **1**.

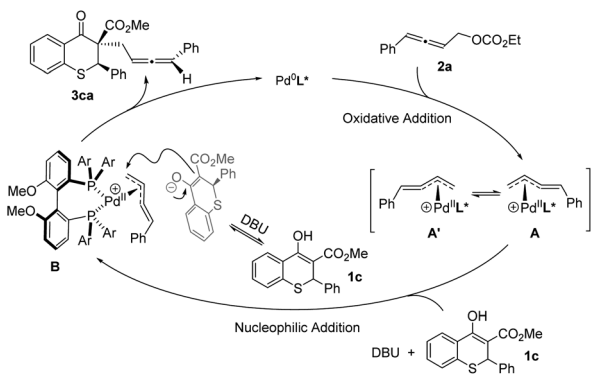


Scheme 4 Substrate scope for the allenylic carbonates **2**

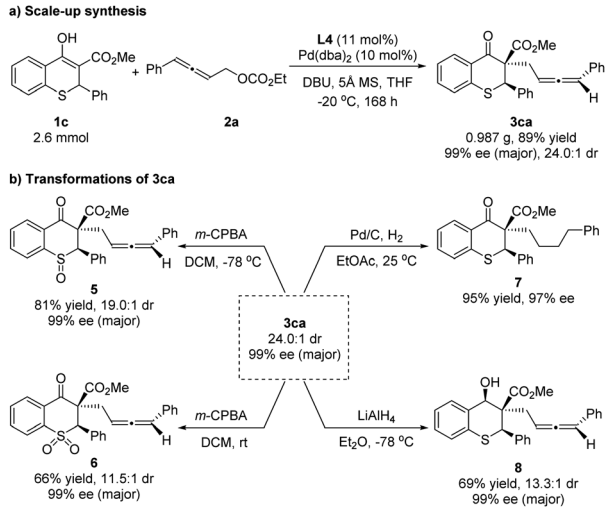
or 4-phenylphenyl as the R, furnishing the product **3ci** or **3cj** in high yield and stereoselectivity. Moreover, allenylic carbonates bearing aromatic substituents, such as naphthyl (**2k**) and thienyl (**2l**), were also suitable substrates. The alkyl substituted allenylic carbonate **2m** also produced the product with a 97% ee value, albeit in 54% yield and 7.3 : 1 dr. In addition, when the trisubstituted allene partner (**2n**) was used, the alkylation reaction underwent smoothly to deliver product **3cn** in 72% yield with 6.7 : 1 dr and 90% ee for the major diastereoisomer at 30 °C, while no reaction was observed at 0 °C.

Based on the above experimental results and the putative mechanism on palladium-catalyzed allenylic alkylation,[9a,e,k] a plausible mechanism was proposed in Scheme 5. First, oxidative addition of racemic allene **2a** formed the π-allylpalladium complexes **A** and **A′**, which were in rapid equilibrium. Subsequently, the nucleophile would attack from the back side of the terminal carbon atom to give the chiral product **3ca**, and regenerate the active Pd(0) species.

To illustrate the practicality of this asymmetric allenylic alkylation reaction, a scale-up synthesis of **3ca** was carried out (Scheme 6a). The product was isolated in 89% yield with 24.0 : 1 dr and 99% ee for the major diastereoisomer under the standard conditions without loss of activity and enantioselectivity. Next, the elaboration of the product was proceeded. The chiral **3ca** could be converted to the corresponding chiral sulfoxide **5** or sulfone **6** using 3-chloroperoxybenzoic acid as the oxidant at different temperatures. Furthermore, the reductions of **3ca** were concentrated on carbonyl and allenyl groups, respectively. The allenyl group could be easily hydrogenated with 10% Pd/C, affording the single reductive isomer **7** in 95% yield and 97% ee, showing that the diastereoselectivity of **3ca** was ascribed to the allene unit. A selective reduction of the carbonyl group of **3ca** with lithium aluminum hydride ($LiAlH_4$) at −78 °C proceeded smoothly, providing the chiral alcohol **8** in 69% yield, 13.3 : 1 dr and 99% ee for the major diastereoisomer (Scheme 6b). The relative configuration of the hydroxyl and



Scheme 5 Plausible mechanism.



Scheme 6 Scale-up synthesis and transformations of **3ca**.

phenyl in compound **8** was assigned as *cis*-**8** by the NOE spectrum (for details, please see the ESI†).

Conclusions

In summary, we have realized the synthesis of enantioenriched multiple substituted thiochromanone derivatives containing two central chiralities and an axial chirality (allene unit) based on the combination of retro-sulfa-Michael addition and palladium-catalyzed asymmetric allenylic alkylation under basic conditions, overcoming the challenges of chemo-, regio- and stereoselectivities. The reaction showed great functional group tolerance, and a broad range of highly enantioenriched products could be conveniently prepared with up to 98% yield, 49.0 : 1 dr and >99% ee. Further investigations utilizing the racemization strategy through retro-hetero-Michael addition on other reactions are being actively pursued in our laboratory.

Data availability

Experimental data has been uploaded as part of the ESI.†

Author contributions

L.-X. L. performed the experiments and prepared the ESI.† Y.-Q. B. and X. L. checked the data. Prof. C.-B. Y. and Y.-G. Z. conceived and directed the project. L.-X. L. and C.-B. Y. prepared the draft and Y.-G. Z. revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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