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# Facile synthesis of sulfinate esters from aryl iodides *via* direct oxidation of thioesters†

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**A practical method to synthesize sulfinate esters from aryl iodides is disclosed. Direct oxidation of thioesters prepared by copper-catalyzed C–S formation of aryl iodides realized the efficient synthesis of sulfinate esters. Due to the good accessibility of aryl iodides, a wide variety of sulfinate esters were prepared from easily available starting materials such as carboxylic acids and anilines.**

Oxidation of thiols is a fundamental method to synthesize a wide range of organosulfurs.[1] For example, disulfides, sulfinic acid esters, and sulfonic acid esters were prepared by oxidation of thiols under different oxidation conditions (Fig. 1A, top).[2–4] Due to the troubling properties of thiols such as unpleasant smell and easy oxidizability under air, the limited preparation of thiols having various functionalities has significantly decreased the accessibility of organosulfurs. Thus, alternative sulfur surrogates instead of thiols have been developed so far for synthesizing highly functionalized organosulfurs.[5] In this study, considering that direct transformations of thioesters as sulfur surrogates can contribute to preparing diverse organosulfurs, we paid attention to developing a new method for synthesizing sulfinic acid esters by direct oxidation of thioesters (Fig. 1A, bottom).

Thioesters have served as protected thiols in the preparation of organosulfurs, where electron-withdrawing acyl groups decrease the nucleophilicity and oxidizability at the sulfur atom.[6] The good stability and accessibility are clear benefits of thioesters as sulfur surrogates in organosulfur synthesis.[7,8] However, the direct oxidation of thioesters is challenging due to their reduced oxidizability and possible overoxidation to organosulfur(VI) compounds.[8b,9,10] Since transformations of sulfinic acid esters allowed us to synthesize highly functionalized sulfoxides and sulfides in our recent studies (Fig. 1B),[11–13] we started to develop an efficient method to prepare sulfinic acid esters through the direct oxidation of thioesters. Herein, we disclose an efficient method to prepare sulfinic acid esters from aryl iodides *via* copper-catalyzed C–S formation followed by direct oxidation of thioesters (Fig. 1C).

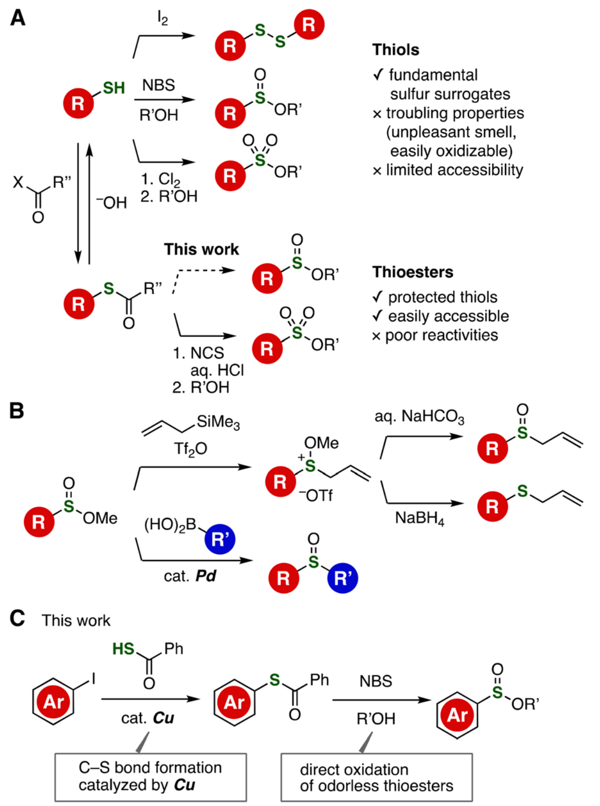

**Fig. 1** (A) Oxidation methods of thiols and thioesters. (B) Transformations of sulfinate esters. (C) This work.

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We first attempted the synthesis of methyl sulfinate **3a** having a tetrasubstituted benzene ring through the oxidation of thiol **2a** in a four-step procedure (Fig. 2A). Indeed, diazotization of aniline **1a**, C–S formation with potassium ethyl xanthate,[14] hydrolysis, and oxidation of the resulting thiol **2a** with *N*-bromosuccinimide (NBS) in methanol afforded sulfinate ester **3a** only in 1% yield. This result obviously indicates that the difficulty in thiol synthesis led to the poor yield, since the preparation of multi-substituted thiols is not always easy.[5] To develop an efficient method to prepare sulfinate esters, we then evaluated frontier orbital energies of thiols **2b** and **2c**, thioesters **4b** and **4c**, and sulfinate esters **3b** and **3c** having a methoxy or a chloro group by DFT calculations (Fig. 2B). These results support the possibility of direct oxidation of thioesters leading to sulfinate esters without overoxidation, since HOMO energies of thioesters **4b** and **4c** are slightly higher than those of sulfinate esters **3b** and **3c**, although oxidation of thioesters **3b** and **3c** will require higher energies than that of thiols **2b** and **2c**. In addition, the electron-donating methoxy group and electron-deficient chloro group significantly affect the HOMO energies. Thus, direct oxidation of thioesters providing sulfinate esters without overoxidation seems to be a challenging issue.

Synthesis of methyl 4-methoxybenzenesulfinate (**3b**) and methyl 4-chlorobenzenesulfinate (**3c**) was accomplished from 4-methoxyphenyl iodide (**5b**) and 4-chlorophenyl iodide (**5c**), respectively, with thiobenzoic acid (**6**) catalyzed by copper under the mild conditions established by Sawada and co-workers[8a] (Fig. 2C). When the thiolation of 4-methoxyphenyl bromide or chloride was attempted, starting materials were recovered, which shows that diverse bromo- or chloro-substituted thioesters can be synthesized by copper-catalyzed thiolation. After screening the reaction conditions, we succeeded in the direct oxidation of *S*-(4-methoxyphenyl) benzothioate (**4b**) with NBS to provide sulfinate ester **3b** efficiently (Table 1, entry 1). To our surprise, sulfinate ester **3b** was not obtained when using NCS[9c] or NIS instead of NBS (entries 2 and 3). While treatment of thioester **4b** with NBA, NBP, or NBSA also afforded sulfinate ester **3b** in good yields, the oxidation of thioester **4b** with DBH,[2a] tetrabutylammonium tribromide, and *m*CPBA resulted in the synthesis of sulfinate ester **3b** in low yields (entries 4–9). In addition, a longer reaction time significantly decreased the yield of **3b** due to overoxidation (entry 10). Not only electron-rich thioester **4b** but also electron-deficient thioester **4c** was successfully oxidized to yield sulfinate ester **3c** efficiently. The yield was not decreased in a gram-scale synthesis of **3c**, indicating the good scalability of this method. We achieved the facile synthesis of sulfinate ester **3c** from thioester **4c** with NBS, NBA, NBP, or NBSA (entries 11, 14, 15, and 16). In contrast, only a trace amount of sulfinate ester **3c** was obtained when thioester **4c** was treated with NCS or NIS (entries 12 and 13). Moreover, the overoxidation of sulfinate ester **3c** by elongation of the reaction time slightly lowered the yield (entry 20). These results clearly show that NBS-facilitated

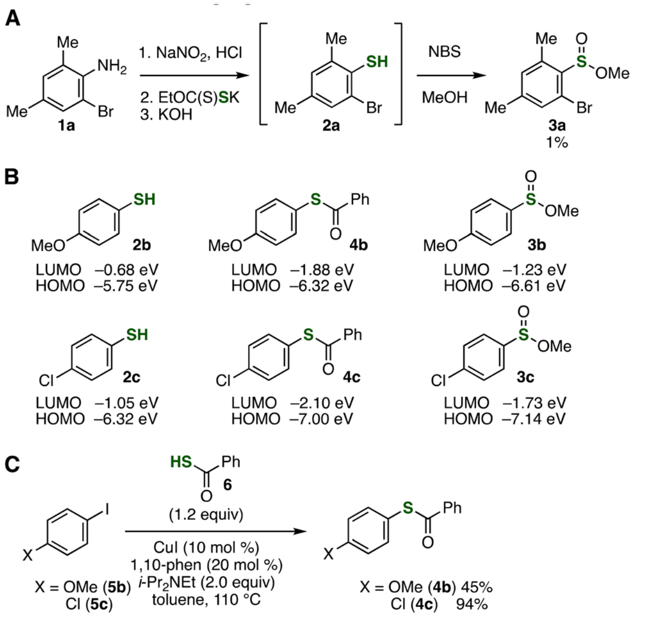
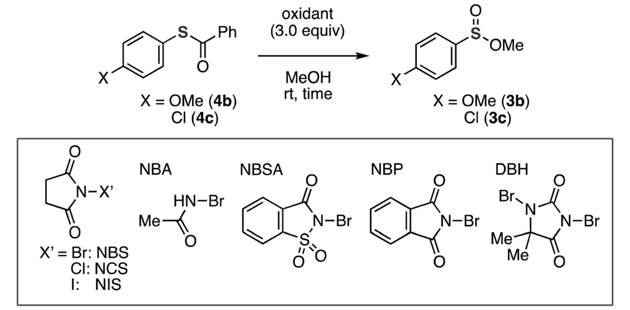


**Fig. 2** (A) An attempt to synthesize **3a**. (B) DFT calculations of **2b**, **2c**, **4b**, **4c**, **3b**, and **3c** (B3LYP/6-311+G(d,p)). See details in the ESI.† (C) Synthesis of **4b** and **4c**. 1,10-phen = 1,10-phenanthroline.

**Table 1** Optimization of the reaction conditions



| Entry | X | Oxidant | Time/h | Yield (%)[a] |
|---|---|---|---|---|
| 1 | OMe | NBS | 1 | 82[b] |
| 2 | OMe | NCS | 1 | Trace |
| 3 | OMe | NIS | 1 | Trace |
| 4 | OMe | NBA | 1 | 54 |
| 5 | OMe | NBP | 1 | 67 |
| 6 | OMe | NBSA | 1 | 80 |
| 7 | OMe | DBH | 1 | 2 |
| 8 | OMe | $n$-$Bu_4NBr_3$ | 1 | 13 |
| 9 | OMe | *m*CPBA | 1 | 3 |
| 10 | OMe | NBS | 18 | 38 |
| 11 | Cl | NBS | 1 | 99[b] [99][b,c] |
| 12 | Cl | NCS | 1 | Trace |
| 13 | Cl | NIS | 1 | Trace |
| 14 | Cl | NBA | 1 | 81 |
| 15 | Cl | NBP | 1 | 94 |
| 16 | Cl | NBSA | 1 | 90 |
| 17 | Cl | DBH | 1 | 58 |
| 18 | Cl | $n$-$Bu_4NBr_3$ | 1 | 20 |
| 19 | Cl | *m*CPBA | 1 | 0 |
| 20 | Cl | NBS | 18 | 65 |

[a] Yields based on $^1H$ NMR analysis. [b] Isolated yields. [c] Gram-scale synthesis. See details in the ESI.†

oxidation allowed us to prepare sulfinate esters **3b** and **3c** having electron-donating and -withdrawing functional groups from odorless thioesters **4b** and **4c**, avoiding overoxidation and without the preparation of thiols.

The 2-step synthesis of sulfinate ester **3c** from aryl iodide **5c** was accomplished using a single silica-gel column chromatography protocol (Fig. 3A). Since easy removal of the smelly thiobenzoic acid (**6**) by a basic aqueous workup allowed us to synthesize sulfinate esters without unpleasant smells, the 2-step protocol for synthesizing sulfinate esters from aryl iodides has a practical advantage over the conventional synthetic method using thiols. We also succeeded in sulfinate ester synthesis through Cu-catalyzed C–S formation of aryl iodides with potassium thioacetate, which was reported by Ho and co-workers,[8b] followed by oxidation with NBS (Fig. 3B). It is worth noting that one-pot synthesis of sulfinate ester **3c** from aryl iodide **5c** was realized in the 2-step sulfinate ester synthesis using potassium thioacetate. Although both thioesters with benzoyl and acetyl groups could lead to sulfinate esters efficiently, good crystallizability of thioesters with benzoyl groups offers an advantage in purification for large-scale synthesis.

A range of sulfinate esters **9a–9c** were successfully synthesized from thioester **4c** by oxidation with NBS in the presence of various alcohols (Fig. 3C). For example, ethanol and 2-methoxyethanol participated in sulfinate ester synthesis when using excess alcohol in dichloromethane. Isopropyl 4-chlorobenzenesulfinate (**9c**) was also prepared using 2-propanol in dichloromethane, in which the yield was improved when 2-propanol was used as a solvent. Unfortunately, the synthesis of *tert*-butyl 4-chlorobenzenesulfinate (**9d**) failed due to the low nucleophilicity of bulky *tert*-butyl alcohol.[15]

We succeeded in the synthesis of diverse sulfinate esters from aryl iodides by Cu-catalyzed C–S formation and subsequent oxidation (Fig. 3D). Benzenesulfinic acid esters **3d–3l** were prepared by the 2-step procedure without damaging methyl, fluoro, bromo, trifluoromethyl, and methoxycarbonyl groups. Of note, we successfully synthesized a wide variety of 2-substituted benzenesulfinate esters **3j–3m** from bulky 2-substituted aryl iodides, where selective C–S formation took place at the iodo group in the presence of a bromo group. It is noteworthy that the preparation of methyl 2-bromothiophene-2-sulfinate (**3n**) was achieved from 2-iodothiophene by the catalytic C–S formation and following oxidation with NBS. Unfortunately, synthesis of methyl 3-pyridylsulfinate was unsuccessful due to the rapid decomposition after the oxidation step.[16] Additionally, we accomplished the synthesis of *S*-alkyl-substituted sulfinate ester **12** from alkyl iodide **10** through a nucleophilic substitution reaction with thiourea and benzoic anhydride, followed by oxidation (Fig. 3E). These results obviously indicate that direct oxidation of thioesters will help in preparing highly functionalized sulfinate esters by virtue of the accessibility and good stability of thioesters.

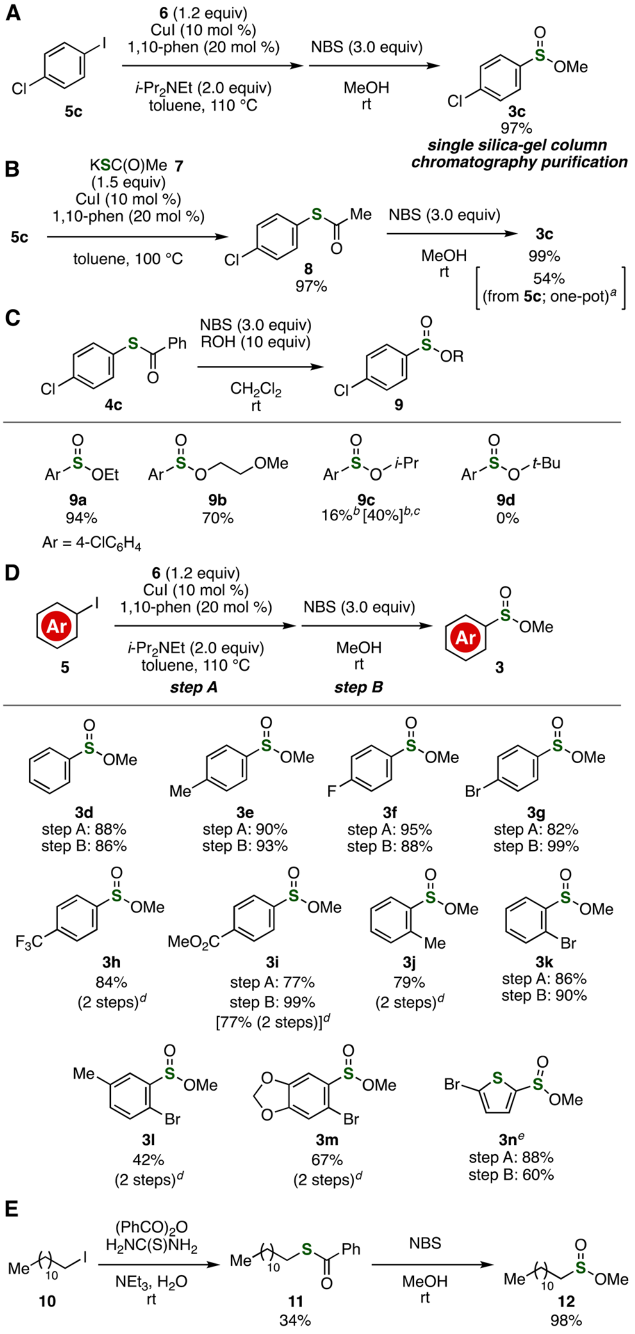


**Fig. 3** (A) Synthesis of **3c** from **5c** by single silica-gel column chromatography purification. (B) Synthesis of **3c** through acetylthiolation of **5c**. (C) Synthesis of sulfinate esters using various alcohols. (D) Synthesis of sulfinate esters from various aryl iodides. (E) Synthesis of **12**. [a] NBS (5.0 equiv.) was used in the oxidation of **8**. [b] Isopropyl alcohol was used as a solvent instead of $CH_2Cl_2$. [c] *S*-(4-Chlorophenyl) thioacetate (**8**) was used instead of thioester **4c**. [d] The synthesis was conducted through single silica-gel column chromatography purification. [e] 2-Iodothiophene was used as a starting material. NBS (4.0 equiv.) was used in step B.

We then conducted control experiments to gain insight into the reaction mechanism of the oxidation of thioesters (Fig. 4A). When thioester **4c** was treated with an equimolar amount of NBS in methanol at room temperature, sulfinate ester **3c** was obtained in a moderate yield. Increasing the amount of NBS to 2.0 or 3.0 equivalents significantly improved the yields of sulfinate ester **3c**, in which sulfinate ester **3c** was

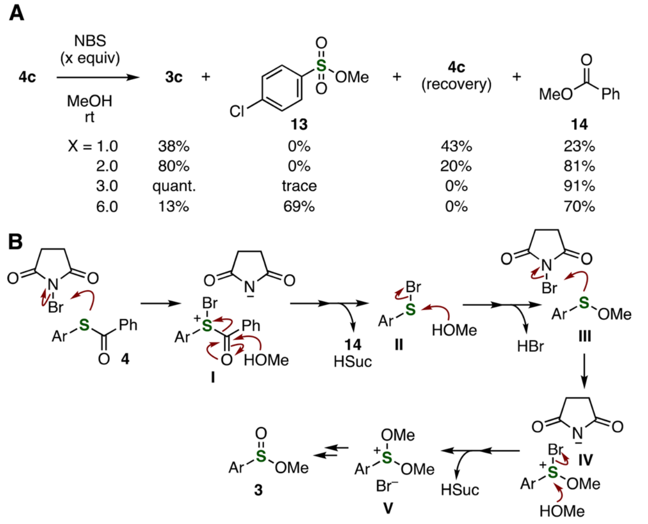


**Fig. 4** (A) Control experiments with varying amounts of NBS. (B) Plausible reaction mechanism.

also synthesized efficiently when using 2.0 equivalents of NBS. The oxidation of thioester **4c** with 6.0 equivalents of NBS resulted in overoxidation of sulfinate ester **3c** to afford sulfonate ester **13** in a high yield. In these reactions, methyl benzoate (**14**) was obtained as a side product. These results show that the oxidation involves reaction steps consuming two molar amounts of NBS.

On the basis of these control experiments, we proposed a reaction mechanism as shown in Fig. 4B, although oxidation mechanisms involving single-electron transfer cannot be excluded.[9] First, direct oxidation of thioester **4** with NBS would take place smoothly. Benzoylation of methanol with intermediate **I** to furnish methyl benzoate can lead to sulfenyl bromide **II**, which would undergo methanolysis to generate sulfenyl ester **III**. Then, the second oxidation of the resulting sulfenyl ester **III** would proceed, followed by further methanolysis to provide sulfinate ester **3**. According to the control experiments using an equimolar amount of NBS, the second oxidation will occur faster than the first oxidation of thioester **4**.

Good accessibility of aryl iodides prompted us to synthesize sulfinate esters from a variety of starting materials (Fig. 5A and B). For example, sulfinate ester **3b** was easily prepared from 4-methoxybenzoic acid (**15**) by decarboxylative iodination,[17] Cu-catalyzed C–S formation, and oxidation with NBS in methanol without isolation of intermediates (Fig. 5A). We also succeeded in the synthesis of sulfinate esters **3a** and **3o–3q** from anilines *via* diazotization, denitrogenative iodination,[18] C–S formation, and oxidation. Since 2-bromoanilines were easily synthesized from the corresponding anilines by electrophilic bromination, these results indicate a synthetic benefit of this newly developed method. It is worth noting that bulky methyl 2-bromo-4,6-dimethylbenzenesulfinate (**3a**) was prepared from 2-bromo-4,6-dimethylaniline through 2-bromo-4,6-dimethylphenyl iodide, clearly showing a great advantage over conventional methods using thiols because only 1% **3a** was synthesized in only 1% from aniline **1a** through thiol **2a** (Fig. 2A).

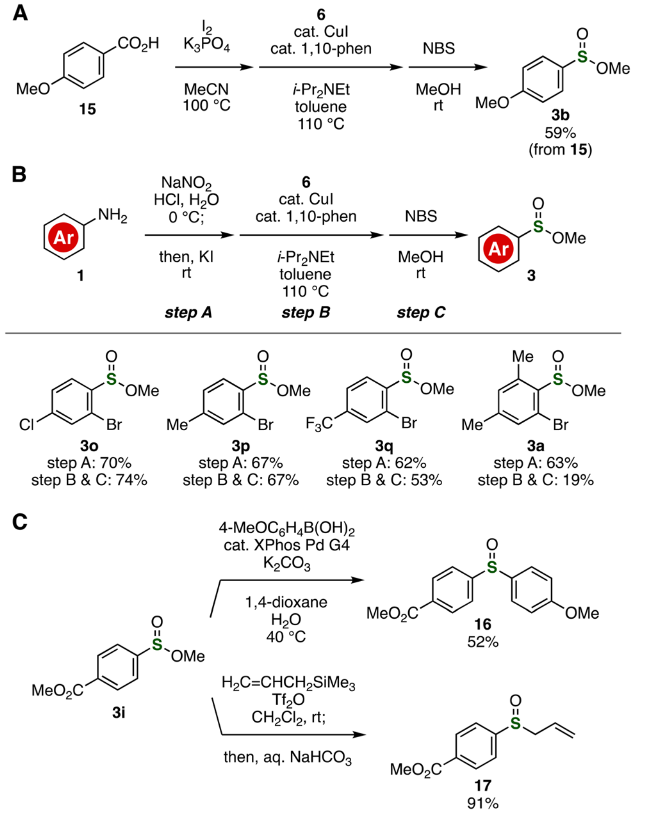


**Fig. 5** (A) Sulfinate synthesis from **15**. (B) Sulfinate synthesis from anilines. (C) Transformations of **3i**.

Compared to conventional preparation methods of sulfinate esters from other sulfur surrogates such as disulfides,[19] superior accessibility of aryl iodides from broad aromatic compounds by not only aromatic electrophilic iodination but also decarboxylative and denitrogenative methods will enable us to synthesize highly functionalized sulfinate esters.

A wide range of organosulfurs such as sulfoxides having functionalities will be synthesized through the sulfinate ester synthesis developed in this study. For instance, we achieved *S*-arylation of sulfinate ester **3i** with 4-methoxyphenylboronic acid catalyzed by palladium (Fig. 5C, top).[13h] Treatment of sulfinate ester **3i** with triflic anhydride in the presence of allyl(trimethyl)silane provided allyl aryl sulfoxide **17**, leaving the methoxycarbonyl group untouched (Fig. 5C, bottom).[13f]

In summary, we have developed a facile synthetic method to synthesize sulfinate esters from aryl iodides. It is worth noting that thioesters were efficiently oxidized, albeit in the presence of an electron-withdrawing carbonyl group on the sulfur atom, to afford sulfinate esters without overoxidation. A wide variety of sulfinate esters were successfully prepared from aryl iodides by the Cu-catalyzed C–S formation and the direct oxidation of the resulting thioesters. Easy removal of thiobenzoic acid by a basic aqueous workup allowed us to synthesize sulfinate esters without unpleasant smells. Due to the good accessibility of aryl iodides[17,18,20] and the diverse synthetic applications of sulfinate esters, the sulfinate ester synthesis developed in this study will be applicable in broad disciplines using organosulfurs. The good accessibility of diverse aryl iodides will be a clear advantage over the conventional sulfinate ester synthesis from thiols. Further studies such as applications in the preparation of bioactive organosulfur derivatives and synthesis of bis-sulfinate esters are underway in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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