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# Base mediated aza-[2 + 1] annulation and regioselective aziridine ring-opening cascade: mild synthesis of functionalized $\beta$ -amino ketones from cyclic *N*-sulfonyl aldimines and $\alpha$ -carbonyl sulfonium salts†

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Cyclic *N*-sulfonyl aldimines are well-known aza-[2C]-synthons for various [2 + *n*] annulation reactions. Herein we describe a novel base mediated [2 + 1] annulation and a regioselective aziridine ring-opening reaction cascade, which provides an efficient and distinct synthetic strategy from readily available cyclic *N*-sulfonyl aldimines and  $\alpha$ -carbonyl sulfonium salts leading to  $\beta$ -amino ketone derivatives through the corresponding fused tri-substituted aziridines. This one-pot, two-step process involves formation of C–C and C–N bonds and subsequent cleavage of a C–N bond. The features of the developed reaction include the use of mild reaction conditions, broad substrate scope, and excellent yields. The synthetic utility of this approach was demonstrated by gram-scale operation and further product derivatizations.

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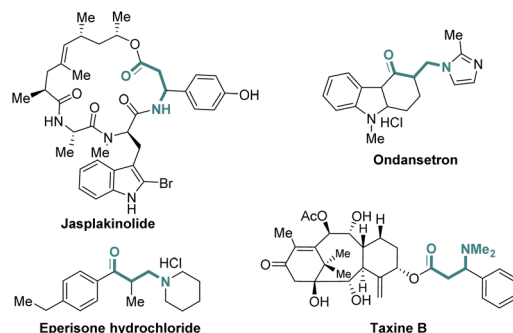
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## Introduction

$\beta$ -Amino ketones ( $\beta$ -AKs) and related derivatives are ubiquitous substructures of many natural products and biologically active molecules (Fig. 1).<sup>1</sup> For example, jaspplainolide is an unusual cyclodepsipeptide natural molecule isolated from *Marine Sponge*, which can be used as an actin polymerization inducer.<sup>1a</sup> Ondansetron is a known drug for the treatment of vomiting caused by chemotherapy.<sup>1b</sup> Eperisone hydrochloride is commonly used to treat spastic paralysis disease.<sup>1c</sup> Taxine B shows potent antiarrhythmic activity.<sup>1d</sup> Furthermore,  $\beta$ -AKs have been also identified as versatile building blocks in organic synthesis. For example, they have been widely used for the synthesis of  $\beta$ -amino alcohols,  $\beta$ -amino acids,  $\beta$ -lactams, 1,3-alkamines, and complex nitrogen-containing natural molecules.<sup>2</sup>

Given their importance and utility in drug discovery and organic synthesis, many methods have been developed for the construction of such scaffolds over the past decades (Scheme 1a). Among them, Mannich-type reactions stand as the most conventional and classical approaches to access  $\beta$ -AKs.<sup>3</sup> In addition, aza-Michael addition reaction of  $\alpha,\beta$ -unsaturated

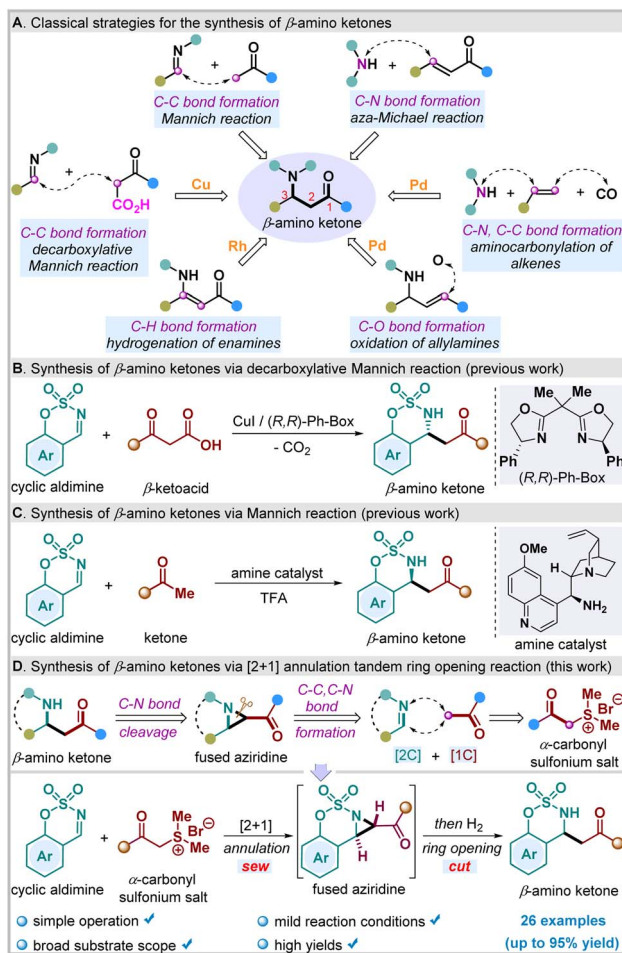
ketones with amine-based nucleophiles represent another reliable protocol to access  $\beta$ -AKs motifs.<sup>4</sup> In parallel, transition metal-catalyzed reactions, such as copper-catalyzed decarboxylative Mannich reaction,<sup>5</sup> palladium-catalyzed amino-carbonylation,<sup>6</sup> rhodium-catalyzed hydrogenation of  $\beta$ -ketoenamides,<sup>7</sup> and palladium-catalyzed Tsuji–Wacker oxidation of internal allyl amines,<sup>8</sup> have been also successfully employed in preparing structurally diverse and synthetically useful  $\beta$ -AKs and their related analogues. Despite great advances have been made for such molecule synthesis, most of those methodologies usually required the use of corresponding pre-functionalized substrates, expensive catalysts, and harsh reaction conditions. From a synthetic standpoint, the development of a novel and mild synthetic strategy for the rapid assembly of  $\beta$ -AKs from easily accessible starting materials is still highly desirable and significant.


 Fig. 1 Representative  $\beta$ -amino ketones-containing compounds.

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Scheme 1 Strategies for the synthesis of  $\beta$ -amino ketones.

Because of their versatile reactivities, sulfamate-derived cyclic aldimines have attracted considerable attention from the synthetic community. Recently, they have been extensively used as electrophiles in various transformations, including alkynylation,<sup>9</sup> allylation,<sup>10</sup> and arylation,<sup>11</sup> *etc.*<sup>12</sup> Additionally, sulfamate-derived cyclic aldimines are also useful building blocks for synthesizing  $\beta$ -Aks.<sup>5,13</sup> For example, Ma and co-workers described a novel Cu-catalyzed asymmetric decarboxylative Mannich reaction of sulfamate-derived cyclic aldimines with  $\beta$ -ketoacids to synthesize  $\beta$ -Aks (Scheme 1b).<sup>5a</sup> The group of Wang reported another asymmetric version of the Mannich reaction to achieve chiral  $\beta$ -Aks from cyclic aldimines using cinchona alkaloid as catalyst (Scheme 1c).<sup>13c</sup> With an electrophilic center (C<sub>1</sub>) and one nucleophilic center (N<sub>2</sub>) arranged consecutively in the same molecule, sulfamate-derived cyclic aldimines often serve as ideal aza-[2C]-synthons in a variety of [2 + 2],<sup>14</sup> [2 + 3],<sup>15</sup> [2 + 4],<sup>16</sup> and [2 + 5]<sup>17</sup> annulations for constructing diverse four- to seven-membered bicyclic *N* heterocycles. However, its potential for fused bicyclic aziridine formation has not been fully explored.<sup>18,13b</sup> The traditional strategies for the synthesis of such type of bicyclic aziridine frameworks mainly rely on the aza-Darzens reactions,<sup>19</sup> copper-catalyzed intramolecular aziridination of unsaturated

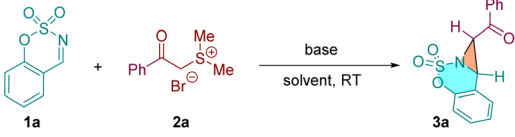
iminoiodinanes,<sup>20</sup> and Rh-catalyzed intramolecular aziridinations of alkenes with sulfamate esters.<sup>21</sup> On the other hand, owing to the intrinsic ring strain, aziridines can be further converted to functionalized linear compounds *via* nucleophilic ring-opening reactions to release the ring strain.<sup>22</sup> In this context, we envisioned that the expected  $\beta$ -AKs could be prepared from the corresponding benzobicyclic sulfamate-fused  $\alpha$ -carbonyl aziridines through hydrogen-mediated reductive ring-opening reactions, whereas the latter in turn could be obtained *via* a novel base mediated [2 + 1] annulations of cyclic aldimines with sulfonium salts (Scheme 1d). However, this cascade synthetic strategy, namely, a “sew-and-cut” approach, is much more challenging and which has not been utilized in the synthesis of  $\beta$ -AKs so far. The majority ring-opening reactions for cyclic sulfamate-fused aziridines typically employ organometallic reagents (*e.g.*, grignard reagents, organolithium reagents) or heteroatom-contained reagents as nucleophiles.<sup>23</sup> Comparably, hydrogen-promoted ring-opening processes are still scarce. Furthermore, different types of ring-opening products (7-membered ring *vs.* 6-membered ring) might be obtained in theory due to regioselectivity of fused aziridines to ring opening.<sup>23b</sup> Therefore, control of the selectivity of this ring-opening reaction is another challenge. Coincidentally, while our research was underway, Lin disclosed a method toward fused aziridines *via* saccharin-derived cyclic ketimines and sulfur ylides under reflux conditions.<sup>24</sup> Herein we describe a cascade [2 + 1] annulation/hydrogen-mediated reductive ring-opening reaction between sulfamate-derived cyclic aldimines and  $\alpha$ -carbonyl sulfonium salts to access  $\beta$ -AKs derivatives under mild conditions.

## Results and discussion

We initially studied the designed [2 + 1] annulation reaction using sulfamate-derived cyclic aldimine **1a** and sulfur ylides precursors dimethyl(2-oxo-2-phenylethyl)sulfonium bromide **2a** as the model substrates (Table 1). Treatment of **1a** with **2a** with potassium carbonate (2.0 equiv.) in dichloromethane at room temperature for 1.5 h, the expected fused aziridine **3a** was obtained smoothly in 96% yield with excellent diastereoselectivity (>20:1 dr) (entry 1). Subsequent various inorganic bases screening demonstrated that sodium carbonate exhibited excellent activity, affording the product in 98% yield (entries 2 and 3). Other inorganic bases, including KOH and NaOH shown comparable catalytic activities to give the [2 + 1] product **3a** in moderate yields (entries 4 and 5). We then investigated a series of organic bases. To our delight, the commonly used base Et<sub>3</sub>N delivered the expected **3a** in nearly quantitative yield with a significant reaction time decrease (entry 8). Finally, the solvent effect on the reaction was examined. It was revealed that the reaction yield was not improved when polar solvents such as THF and CH<sub>3</sub>CN were used as the reaction medium (entries 9 and 10).

With the optimized reaction conditions in hand, the scope of this [2 + 1] annulation reaction was examined. As shown in Table 2, a variety of cyclic aldimines reacted smoothly with  $\alpha$ -carbonyl sulfonium salt **2a** to furnish the corresponding



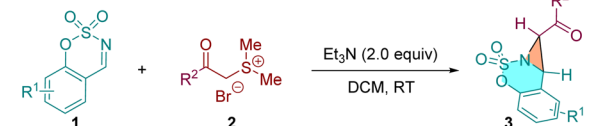
Table 1 Optimization of the reaction conditions<sup>ab</sup>


Entry	Base	Solvent	Time (h)	Yield (%)
1	K <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	15	96
2	CS <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	15	82
3	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	24	98
4	KOH	CH <sub>2</sub> Cl <sub>2</sub>	3	75
5	NaOH	CH <sub>2</sub> Cl <sub>2</sub>	3	77
6	DMAP	CH <sub>2</sub> Cl <sub>2</sub>	24	41
7	DBU	CH <sub>2</sub> Cl <sub>2</sub>	0.5	Trace
8	Et <sub>3</sub> N	CH <sub>2</sub> Cl <sub>2</sub>	1.5	99
9	Et <sub>3</sub> N	THF	1.5	83
10	Et <sub>3</sub> N	CH <sub>3</sub> CN	1.5	86

<sup>a</sup> Reaction conditions: **1a** (0.40 mmol), **2a** (0.6 mmol) and base (0.80 mmol) in solvent (3.0 mL). <sup>b</sup> Isolated yield. DMAP = 4-dimethylaminopyridine. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. THF = tetrahydrofuran.

products in excellent yields (**3a–3n**, 73–99% yields). Cyclic aldimines bearing both electron-donating groups (–Me, –OMe, –<sup>t</sup>Bu) and electron-withdrawing groups (–F, –CF<sub>3</sub>, –Cl, –Br, –CO<sub>2</sub>Me) on the phenyl ring were all well tolerated under identified conditions. It was found that the substitution position of the substituents on the cyclic aldimines has notable influence on the efficiency of this [2 + 1] annulation. For example, the *ortho*- and *meta*-substituted aldimines delivered the desired products **3e** and **3f** in moderate yields (74% and 73%), while the *para*-substituted substrate gave **3g** in 97% yield. The methylated ketimine provided **3o** only in 12% yield, and the phenyl group substituted ketimine did not afford the desired bicyclic aziridine probably due to the steric effect (structure not shown). Notably, the saccharin-derived imine substrate **3p**, which has proven to be suitable reactant in various annulations,<sup>24</sup> did not give the expected product under our conditions. We then investigated the scope of the  $\alpha$ -carbonyl sulfonium salts. A range of substrates bearing diverse substituents on the phenyl ring were all compatible to the current reaction conditions (**3q–3y**). The CF<sub>3</sub> substituted substrate gave a slightly lower yield (**3z**). Beyond phenyl, 1-naphthyl and 1-thienyl derived sulfonium salts were also applicable to this reaction (**3aa** and **3ab**).

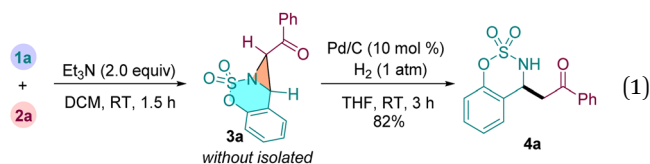
We then turned our attention to explore our designed cascade reactions to synthesize  $\beta$ -AKs from **1a** and **2a** by one-pot procedure (eqn (1)). Thus, treatment of cyclic aldimine **1a** with  $\alpha$ -carbonyl sulfonium salt **2a** under standard conditions afforded the fused aziridine **3a**. Then, the solvent dichloromethane was evaporated and the crude product **3a** was directly redissolved in tetrahydrofuran without isolation. Finally, the reaction mixture further stirred at room temperature for 3 h in the presence of Pd/C (10 mol%) under hydrogen atmosphere (1 atm). Gratifyingly, the expected  $\beta$ -amino ketone **4a** was isolated in 82% yield based on **1a**. This result shows that our designed tandem strategy was feasible for preparing  $\beta$ -AKs.

Table 2 Substrate scope of the [2 + 1] annulation of cyclic imines and sulfonium salts<sup>ab</sup>


<b>3a</b> : 99%	X-ray of <b>3a</b>	<b>3b</b> : 99%	<b>3c</b> : 94%
<b>3d</b> : 77%	<b>3e</b> : 74%	<b>3f</b> : 73%	<b>3g</b> : 97%
<b>3h</b> : 99%	<b>3i</b> : 76%	<b>3j</b> : R = F, 88% <b>3k</b> : R = CF <sub>3</sub> , 43%	<b>3l</b> : 96%
<b>3m</b> : 93%	<b>3n</b> : 96%	<b>3o</b> : 12%	<b>3p</b> : 0%
<b>3q</b> : 92%	<b>3r</b> : 97%	<b>3s</b> : 99%	<b>3t</b> : 99%
<b>3u</b> : 95%	<b>3v</b> : 94%	<b>3w</b> : 96%	<b>3x</b> : 70%
<b>3y</b> : 80%	<b>3z</b> : 41%	<b>3aa</b> : 98%	<b>3ab</b> : 98%

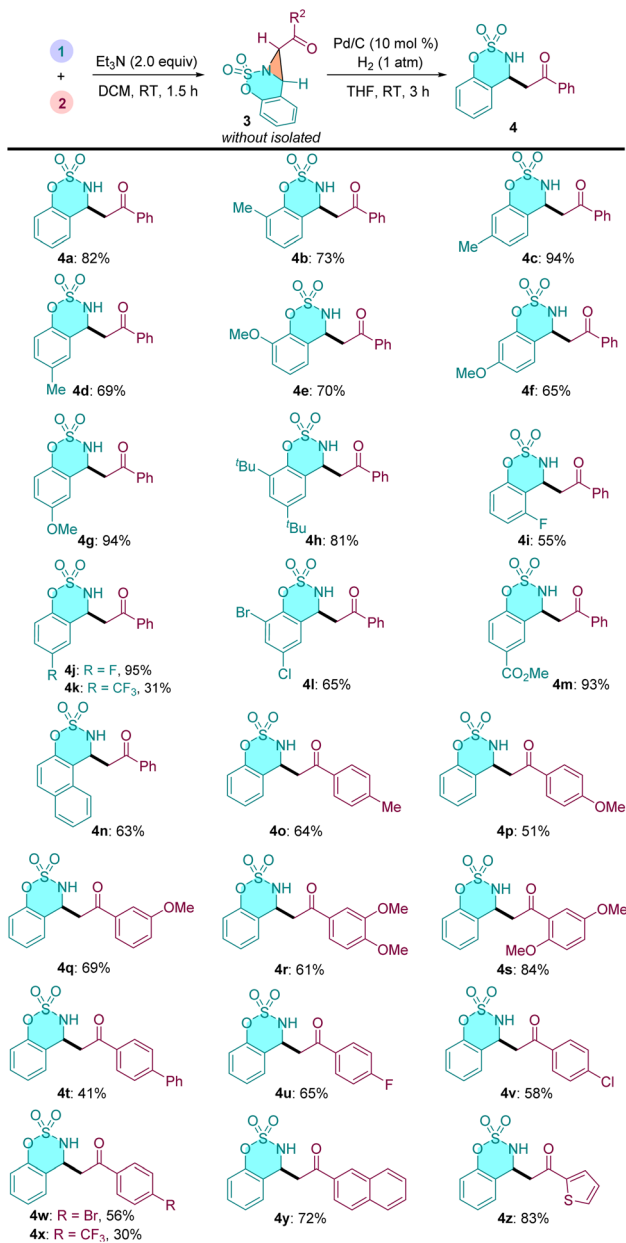
<sup>a</sup> Reaction conditions: **1** (0.40 mmol), **2** (0.60 mmol) and base (0.80 mmol) in dichloromethane (3.0 mL) at RT for 1.5 h. <sup>b</sup> Isolated yield.





Next, we explored the substrate scope and generality of this one-pot sequential reaction (Table 3). In general, a series of cyclic aldimines and  $\alpha$ -carbonyl sulfonium salt smoothly

**Table 3** Substrate scope of the [2 + 1] annulation tandem reductive ring-opening reactions<sup>ab</sup>



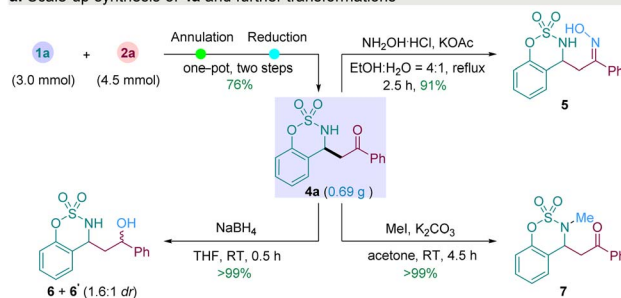
<sup>a</sup> Reaction conditions: **1** (0.40 mmol), **2** (0.60 mmol) and base (0.80 mmol) in dichloromethane (3.0 mL) at RT for 1.5 h; then the solvent was exchanged to tetrahydrofuran and further stirred at RT for 3 h under Pd/C (10 mol%), H<sub>2</sub> (1 atm) conditions. <sup>b</sup> Isolated yield.

participated in this cascade process under the standard conditions, affording the desired  $\beta$ -amino ketones in moderate to good yields. The electronic property of the substituent on the cyclic aldimine moieties had some impact on this reaction efficiency. For example, cyclic aldimines bearing electron-donating substituents generally gave higher yields than those with electron-withdrawing groups (**4b–4h** vs. **4i–4l**). *Meta*-methoxy substituted aldimine **4f** resulted a slightly lower yield because of an over-reduction byproduct was observed. Similarly,  $\alpha$ -carbonyl sulfonium salts with diverse functional groups led to the corresponding  $\beta$ -AKs **4o–4x** in moderate to good yields. Some other aromatic rings, such as **4y–4z** also can be incorporated into the products.

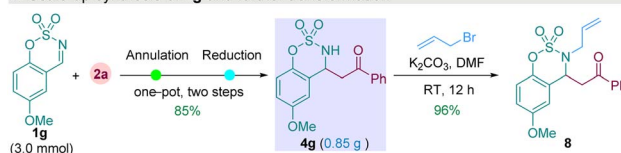
To demonstrate the synthetic utility of this approach, several transformations of products were carried out (Scheme 2). A 3.0 mmol scale reactions were conducted, **4a** (0.69 g) and **4g** (0.85 g) were obtained in good yields (Scheme 2a). Subjecting  $\beta$ -amino ketone **4a** with hydroxylamine hydrochloride delivered the corresponding ketoxime **5** in 91% yield. The carbonyl group of **4a** was reduced by sodium borohydride to generate alcohols **6** and **6'** in 99% yield (1.6:1 dr). Treatment of **4a** with iodomethane under basic condition afforded methylated **7** in nearly quantitative yield. The free amino group of the **4g** was protected by treatment with allyl bromide.

Based on the previous reports and the above results, a plausible mechanism is described in Scheme 3. In the presence of

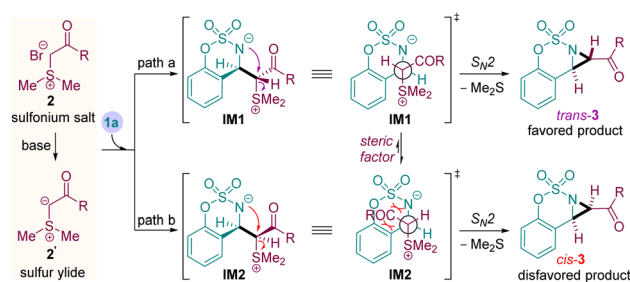
**a.** Scale-up synthesis of **4a** and further transformations



**b.** Scale-up synthesis of **4g** and further transformation



**Scheme 2** Synthetic applications.



**Scheme 3** Plausible mechanism.



base, the  $\alpha$ -carbonyl sulfonium salt **2** undergoes one molecule of hydrobromic acid elimination to form the sulfur ylide **2'**. Then, the ylide **2'** attacks the electron-deficient cyclic aldimine **1a** to give the zwitterion intermediates IM1 and IM2 through two possible pathways (path a and b). Subsequent intramolecular  $S_N^2$  nucleophilic substitution reaction proceeds through the less steric effect intermediate IM1 leads to the *trans*-trisubstituted fused-aziridine product **3**.

## Conclusions

In summary, we have developed a novel base-promoted formal [2 + 1] annulation reaction of cyclic *N*-sulfonyl aldimines with  $\alpha$ -carbonyl sulfonium salts for the efficient synthesis of bicyclic fused aziridines. With hydrogen as nucleophile, these fused trisubstituted aziridines can be readily transformed to  $\beta$ -amino ketone derivatives in good to excellent yields through ring-opening reactions. Different from the conventional strategies, the developed protocol provides a distinct "sew-and-cut" strategy for the rapid access of  $\beta$ -amino ketones by the strategic utilization of the cascade reactions. This one-pot, two-steps process involves creation of C–C and C–N bonds and subsequent selectivity cleavage of a C–N bond. The mild reaction conditions enabled such reaction to be compatible with a broad range of functional groups. The synthetic utility of this chemistry was demonstrated by gram-scale operation and further products derivatizations.

## Author contributions

X. Lei and J. Shi conceived and directed the project. X. Lei designed experiments and X. Lei and Y. Sun performed experiments, analysed the experimental data. X. Lei wrote the manuscript and J. Shi revised the manuscript. Q. Guo discussed the results.

## Conflicts of interest

There are no conflicts to declare.

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