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Silver-Catalyzed Decarboxylative Chlorination of Aliphatic Carboxylic Acids

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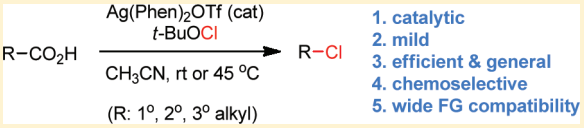
Supporting Information

ABSTRACT: Decarboxylative halogenation of carboxylic acids, the Hunsdiecker reaction, is one of the fundamental functional group transformations in organic chemistry. As the initial method requires the preparations of strictly anhydrous silver carboxylates, several modifications have been developed to simplify the procedures. However, these methods suffer from the use of highly toxic reagents, harsh reaction conditions, or limited scope of application. In addition, none is catalytic for aliphatic carboxylic acids. In this Article, we report the first catalytic Hunsdiecker reaction of aliphatic carboxylic acids. Thus, with the catalysis of $Ag(Phen)_2OTf$, the reactions of carboxylic acids with *t*-butyl hypochlorite afforded the corresponding chlorodecarboxylation products in high yields under mild conditions. This method is not only efficient and general, but also chemoselective. Moreover, it exhibits remarkable functional group compatibility, making it of more practical value in organic synthesis. The mechanism of single electron transfer followed by chlorine atom transfer is proposed for the catalytic chlorodecarboxylation.



INTRODUCTION

Decarboxylative halogenation of carboxylic acids, the Hunsdiecker reaction, is one of the fundamental functional group transformations in organic chemistry.[1−4] The initial discovery by Borodine[5] and Hunsdiecker[6] used dry silver(I) salts of aliphatic carboxylic acids to react with bromine, resulting in the formations of alkyl bromides of one-carbon shorter. Because of the difficult preparation of anhydrous silver carboxylates, several methods have thereafter been developed to simplify the procedure. For example, the much more stable thallium(I) or mercury(II) salts can be utilized instead of silver(I) salts.[6−8] The combination of red HgO and halogen allows the direct use of carboxylic acids as the substrates (Cristol−Firth modification).[9] To avoid the use of highly toxic reagents, Suárez et al. introduced the iododecarboxylation of carboxylic acids with (diacetoxy)iodobenzene and I_2 under UV photolysis, the Suárez modification.[10] This metal-free method shows an excellent performance in the iododecarboxylation of primary alkyl carboxylic acids. However, the reactions of tertiary alkyl carboxylic acids result in the formation of alkenes rather than tertiary iodides.[10] The above methods, along with their variants,[11−13] all proceed via the intermediacy of acyl hypohalites (Figure 1). A different approach is the treatment of aliphatic carboxylic acids with $Pb(OAc)_4$ and lithium halides, the Kochi modification,[14−16] which works well for all of the primary, secondary, and tertiary alkyl acids. However, the drawback is also obvious in that excess carboxylic acids have to be used and the yields are based on the amount of $Pb(OAc)_4$. Another method of halodecarboxylation involves the decomposition of thiohydroxamate esters (Barton esters) in halogen donor solvents such as $BrCCl_3$ or CHI_3, the Barton modification,[17−21] which exhibits an excellent functional group tolerance and has found important application in natural product synthesis.[22] Nevertheless, the Barton modification requires the preparations of the Barton esters, and the halodecarboxylation also produces the undesired 2-(alkylthio)-pyridine as the side-product. In general, besides suffering from either harsh reaction conditions or the use of highly toxic reagents or limited scope of applications, none of these methods is catalytic. It is worth mentioning that a number of methods[23−37] have been reported for the decarboxylative halogenation of aromatic α,β-unsaturated carboxylic acids, some of which are even catalytic.[23−28] However, they proceed via nonradical processes and are not applicable to aliphatic carboxylic acids. It is therefore highly desirable to develop more economical and practical methods for the decarboxylative halogenation. Herein, we report that, under the catalysis of a

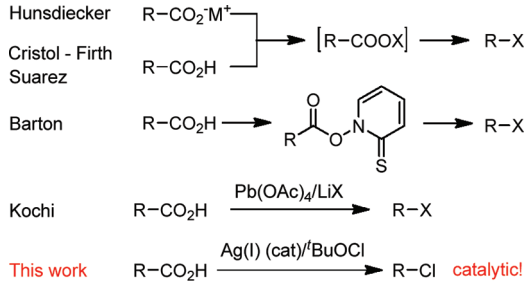


Figure 1. Overview of radical Hunsdiecker-type reactions.

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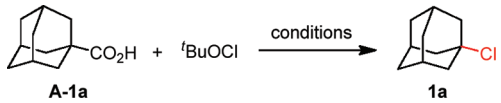
Table 1. Decarboxylative Chlorination of Acid A-1a



A-1a 1a

entry[a]	catalyst[b]	solvent	time (h)	yield (%)[c]
1	$Ag(Phen)_2OTf$ (5)	CH_3CN	24	88
2	AgOTf (10)	CH_3CN	24	0
3	Phen (10)	CH_3CN	24	0
4	none	CH_3CN	24	0
5	$Ag(BPy)_2OTf$ (5)	CH_3CN	24	81
6	$Ag(TMPhen)_2OTf$ (5)	CH_3CN	24	90
7	$Ag(Phen)_2OTf$ (5)	CH_2Cl_2	24	62
8	$Ag(Phen)_2OTf$ (5)	$PhCH_3$	24	0
9	$Ag(Phen)_2OTf$ (5)	THF	24	0
10	$Ag(Phen)_2OTf$ (5)	acetone	24	41
11	$Ag(Phen)_2OTf$ (5)	CH_3CN	3	93
12[d]	$Ag(Phen)_2OTf$ (5)	CH_3CN	1	82

[a]Reaction conditions: **A-1a** (1.0 mmol), *t*-BuOCl (1.5 mmol), solvent (10 mL), catalyst, room temperature. [b]Phen, 1,10-phenanthroline; BPy, 2,2′-bipyridine; TMPhen, 3,4,7,8-tetramethyl-1,10-phenanthroline. [c]Isolated yield based on **A-1a**. [d]Na_2CO_3 (1.0 mmol) was added.

silver(I) complex, the reactions of aliphatic carboxylic acids with *tert*-butyl hypochlorite led to the efficient and general decarboxylative chlorination under mild conditions (Figure 1).[38]

RESULTS AND DISCUSSION

Our approach originated from the use of ligands. Because ligands play a key role in various transition metal-catalyzed reactions, we envisioned that a certain type of Ag(I) complexes might be able to catalyze the Hunsdiecker reaction. To test this idea, adamantane-1-carboxylic acid (**A-1a**) was chosen as the model substrate, and the readily available silver triflate–bis(1,10-phenanthroline) complex,[39] $Ag(Phen)_2OTf$, was chosen as the catalyst to screen the suitable halogenating agents. The use of I_2, Br_2, or *N*-iodo-, *N*-bromo-, or *N*-chlorosuccinimide, with or without the aid of a base such as Na_2CO_3, failed to give any expected halodecarboxylation products in refluxing 1,2-dichloroethane or acetonitrile. However, when *tert*-butyl hyperchlorite, the stable and easily available (from the reaction of *tert*-butanol with sodium hypochlorite) chlorinating agent, was used, we were delighted to find that the corresponding decarboxylative chlorination product 1-chloroadamantane (**1a**) was observed. Thus, with *t*-BuOCl as the chlorine source, we went on to optimize the reaction conditions (Table 1). In the presence of 5 mol % $Ag(Phen)_2OTf$, the treatment of **A-1a** with *t*-BuOCl in CH_3CN at room temperature for 24 h led to the formation of the product **1a** in 88% yield (entry 1, Table 1). The catalytic effect of the silver complex was further confirmed by the control experiments with either AgOTf or the ligand 1,10-phenanthroline (Phen) (entries 2–4, Table 1). Switching the ligand to 2,2′-bipyridine (BPy) or 3,4,7,8-tetramethyl-1,10-phenanthroline (TMPhen) gave similar results (entries 5 and 6, Table 1). The reaction gave a lower product yield in dichloromethane or acetone, while no product could be observed in toluene or THF (entries 7–10, Table 1). Careful monitoring of the reaction revealed that, with the catalysis of $Ag(Phen)_2OTf$, the acid **A-1a** was in fact all consumed within 3 h, and the product **1a** was thus isolated in 93% yield (entry 11, Table 1). The addition of a base such as Na_2CO_3 speeded up the decarboxylation. However, the yield of **1a** was not improved (entry 12, Table 1).

With the optimized conditions in hand (entry 11, Table 1), we went on to examine the scope and limitation of this method (Table 2). As shown in Table 2, tertiary alkyl carboxylic acids underwent efficient decarboxylative chlorination at room temperature, providing the expected chlorides **1a–1f** in excellent yields within 3 h. The chlorodecarboxylation of secondary alkyl carboxylic acids also proceeded smoothly at room temperature, leading to the synthesis of the corresponding chlorides **2a–2g** in satisfactory yields, albeit a longer reaction time (11–24 h) was required for the completion of reaction. The decarboxylation of arylacetic acids also occurred at room temperature to give the substituted benzyl chlorides **3a–3h**. Note that the reaction of *p*-nitrophenylacetic acid (to give **3d**) took a longer time than that of *p*-chloro- or *p*-methyl-substituted phenylacetic acid (to give **3a** or **3b**). Allylic carboxylic acids showed a behavior similar to that of arylacetic acids as exemplified by the generation of allylic chloride **4**. Analogously, protected α-hydroxy or α-amino acids readily underwent chlorodecarboxylation to give the corresponding chlorides **5a–5c**. Racemic product **5c** was obtained from the reaction of optically pure N-protected (*S*)-phenylalanine.

As compared to tertiary or secondary alkyl carboxylic acids, primary alkyl carboxylic acids are much less reactive. For example, the reaction of stearic acid (**A-6a**) under the optimized conditions gave only a trace amount of expected product. However, when the reaction was carried out at a higher temperature (45 °C), the product 1-chloroheptadecane (**6a**) was obtained in 33% yield. Increasing the amount of silver catalyst to 10 mol % resulted in the much higher yield of product (88%). Thus, a number of primary alkyl carboxylic acids were subjected to the treatment with *t*-BuOCl at 45 °C with the catalysis of 10 mol % $Ag(Phen)_2OTf$, and the corresponding chlorides **6a–6e** were secured in satisfactory yields (Table 2). Again, the addition of Na_2CO_3 speeded up the decarboxylation as exemplified by the formation of **6c** (80%) within 2 h. On the other hand, aromatic acids such as 4-chlorobenzoic acid (**A-7a**) and 2,4-dichlorobenzoic acid failed to give any desired products under the above experimental conditions, while all of the starting acids were recovered.

The results in Table 2 have clearly demonstrated the generality of this new method. It can also be seen that the

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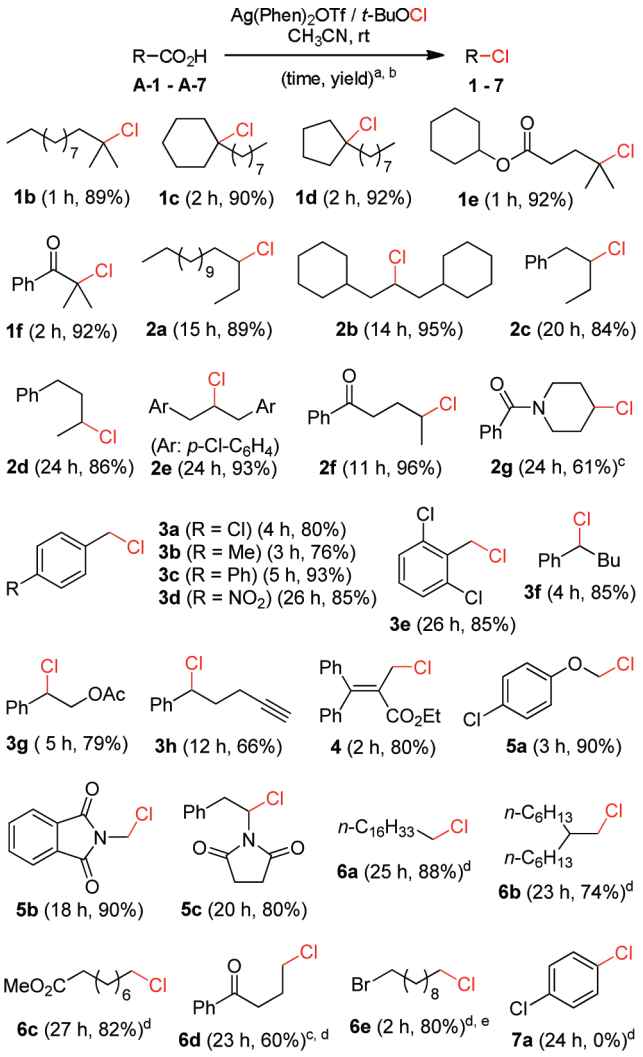
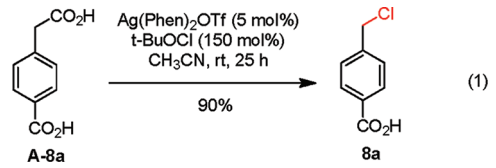
Table 2. Silver-Catalyzed Decarboxylative Chlorination of Carboxylic Acids

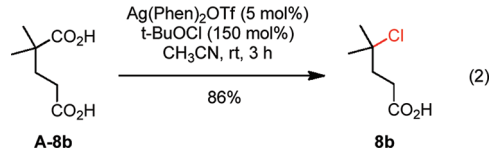


[a]Reaction conditions: carboxylic acid (0.50 mmol), $Ag(Phen)_2OTf$ (0.025 mmol), *t*-BuOCl (0.75 mmol), CH_3CN (5 mL), room temperature. [b]Isolated yield based on the starting carboxylic acid. [c]30% of the carboxylic acid was recovered. [d]The reaction was carried out at 45 °C with the use of 10 mol % of $Ag(Phen)_2OTf$. [e]The reaction was carried out in the presence of Na_2CO_3 (300 mol %).

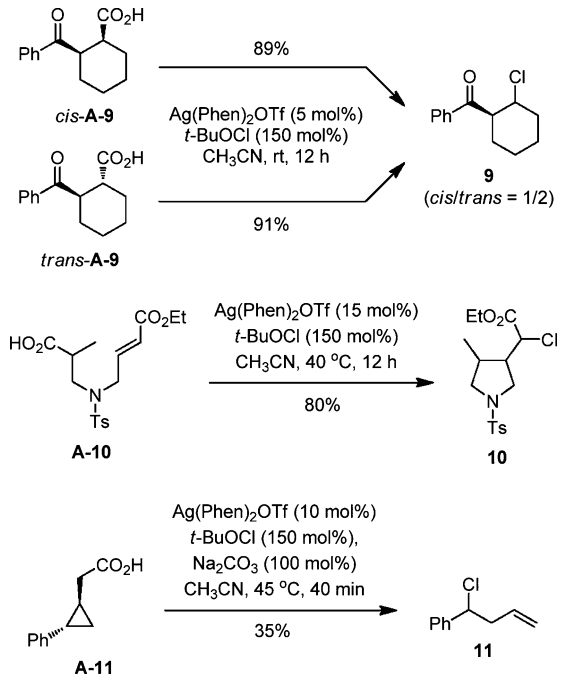
reactivities of carboxylic acids decrease in the order of benzyl ≈ tertiary > secondary > primary ≫ aromatic. This reactivity pattern also allows the successful implementation of chemoselective chlorodecarboxylation. For example, the benzylic carboxyl group in diacid **A-8a** was selectively removed to provide the benzyl chloride **8a**, while the benzoic carboxyl group remained intact, as shown in eq 1. Similarly, 2,2-dimethylpentanedioic acid (**A-8b**) underwent chemoselective decarboxylation to give the tertiary alkyl chloride **8b** exclusively (eq 2). The catalytic processes also enjoy the tolerance of a wide variety of functional groups, including amide, ester, carbonyl, alkene, alkyne, halide, ether, and nitro groups, etc. Nevertheless, functional groups such as hydroxyl, amino, and electron-rich aryl groups bearing strong electron-donating substituents are not compatible because of the electrophilic nature of *tert*-butyl hypochlorite.

To shed light on the mechanism of the above reactions, we designed the following experiments (Scheme 1). Both *trans*-





Scheme 1. Mechanistic Insights on the Decarboxylative Chlorination



(*trans*-**A-9**) and *cis*-2-benzoylcyclohexanecarboxylic acids (*cis*-**A-9**) led to the same formation of chloride **9** as the mixture of two stereoisomers in a 1:2 ratio under the same reaction conditions. In the case of substituted hept-6-enoic acid **A-10**, the decarboxylation was followed by 5-*exo* cyclization prior to chlorination, and pyrrolidine **10** was thus obtained in 80% yield as the mixture of four stereoisomers in 18:14:38:30 ratio determined by LC–MS. Finally, cyclopropylacetic acid **A-11** was used as the radical "clock" to probe the mechanism.[40] The reaction of **A-11** in the presence of Na_2CO_3 afforded the ring-opening product **11** in 35% yield along with 30% of the substrate **A-11** recovered. No 1-chloromethyl-2-phenylcyclopropane could be detected. These results all support the involvement of free radical mechanism in the silver-catalyzed processes.

While the detailed mechanism is not clear and the intermediacy of mononuclear silver species such as *t*-BuOAg(III)Cl (presumably via oxidative insertion) cannot be excluded at this moment, a tentative mechanism is proposed as shown in Figure 2. The oxidation of Ag(I) complex by *t*-BuOCl leads to the generation of the dinuclear Ag(II) complex **A** presumably bridged by chloride and *tert*-butoxide. The intermediate **A** undergoes the ligand exchange upon treatment with an

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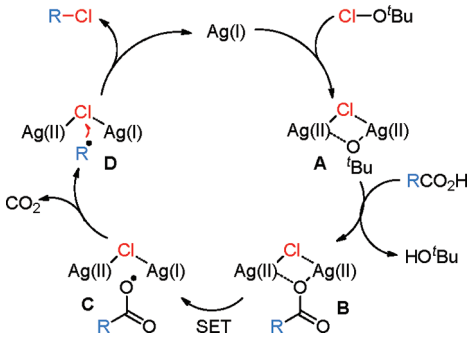

Figure 2. Proposed mechanism for Ag(I)-catalyzed decarboxylative chlorination.

aliphatic carboxylic acid to give species **B**. The carboxylate anion in **B** is then oxidized by an adjacent Ag(II) to give the carboxyl radical (**C**), which undergoes fast decarboxylation to generate the alkyl radical (**D**). The alkyl radical then abstracts the chlorine atom of Ag(II)−Cl to afford the product alkyl chloride, and the Ag(I) complex is regenerated, which enters into the next catalytic circle. Thus, the silver-catalyzed decarboxylative chlorination is likely a process of single electron transfer followed by chlorine atom transfer.

The oxidation potential of $Ag(Phen)_2^+$ is about 1.39 V.[41] While the reduction potential of *t*-BuOCl is not available, it is expected to be close to the reduction potential of ClO^- (1.49 V).[42] These data support our hypothesis of the oxidation of $Ag(Phen)_2^+$ by *t*-BuOCl. Indeed, when the CH_3CN solution of $Ag(Phen)_2OTf$ was treated with *t*-BuOCl, the pale yellow solution immediately turned to red brown, implying the generation of Ag(II) complexes.[43] On the other hand, no color change could be observed when $Ag(Phen)_2OTf$ was treated with a weaker oxidant such as NCS or NBS. These observations might also explain the inactiveness of NCS or NBS in the above halodecarboxylation (vide supra).

The oxidation of carboxylate anions by Ag(II) complexes is well documented.[44−46] The above-mentioned reactivity pattern of carboxylic acids strongly supports the oxidative decarboxylation.[19] The transition metal-assisted chlorine atom transfer, that is, the trap of an alkyl radical by a complexed metal chloride in the higher oxidation state ($M^{n+1}L_mCl$) to give the alkyl chloride and metal complex in the lower oxidation state (M^nL_m), is also well-known.[47−49] These processes can be catalyzed by a number of transition metals such as complexes of Ru,[47] Cu,[48,49] Fe,[50] or Ni,[51] which in turn support our hypothesis of Cl-abstraction from Ag(II)−Cl.

A number of chloride-[52−63] or oxygen-bridged[64−70] (including carboxylate-bridged[67−70]) dinuclear silver(I) complexes with Ag_2Cl_2 or Ag_2O_2 core structures have been reported, which lead to our assumption of the transient species **A** and **B**. The addition of a base may help the ligand exchange from **A** to **B**, consistent with the observation of the acceleration of chlorodecarboxylation by Na_2CO_3. Mixed-valent Ag(II)/Ag(I) complexes are also known in the literature.[71−76] It is worth mentioning that, while the direct reaction of acid **A-1a** with $Ag(Phen)_2S_2O_8$ (2 equiv) in CH_3CN/H_2O at room temperature led to the complete decarboxylation of **A-1a**, the treatment of **A-1a** with $Ag(Phen)_2S_2O_8$ (2 equiv) and LiCl (1 or 2 equiv) in CH_3CN or CH_3CN/H_2O (1:1, v:v) at room temperature for 24 h did not give any desired chloride **1a**, and most starting material **A-1a** (>85%) was recovered. Switching LiCl to NaCl showed no difference. These results imply that mononuclear complexes $Ag(Phen)_2Cl_2$ or $Ag(Phen)_2Cl^+$ cannot be the active species in the chlorodecarboxylation of acids with *t*-BuOCl. Further mechanistic investigations are required to reveal the nature of the high-valent silver intermediates.

An alternative mechanism is that the alkyl radical may abstract a chlorine atom from *t*-BuOCl to give alkyl chloride and a *tert*-butoxyl radical. The oxidation of Ag(I) to Ag(II) by the *tert*-butoxyl radical followed by Ag(II)-mediated decarboxylation regenerates an alkyl radical, which enters into the next catalytic circle. To test this hypothesis, acid **A-1a** was treated with $Ag(Phen)_2OTf$ (20 mol %) and a stoichiometric amount of di-*tert*-butyl peroxyoxalate (DBPO)[77,78] as the *tert*-butoxyl radical source in CH_3CN at room temperature. While DBPO gradually decomposed, no decarboxylation occurred and all **A-1a** remained unchanged. No color change could be observed when mixing DBPO with $Ag(Phen)_2OTf$ in acetonitrile at room temperature, implying that *tert*-butoxyl radical is unable to oxidize the Ag(I) complex. Furthermore, the UV photolysis of carboxylic acids with *t*-BuOCl led to the formation of chlorinated carboxylic acids (rather than decarboxylation) via the *tert*-butoxyl radical intermediacy, as reported by Shigemitsu et al.[79] These all suggest that *tert*-butoxyl radicals are unlikely to be involved in the silver-catalyzed chlorodecarboxylation with *t*-BuOCl.

■ CONCLUSION

We have developed the first Ag(I)-catalyzed decarboxylative chlorination of aliphatic carboxylic acids with *tert*-butyl hypochlorite. This method is mild, efficient, and chemoselective. In view of its generality and excellent functional group compatibility, this catalytic transformation should find practical applications in organic synthesis.

■ EXPERIMENTAL SECTION

Typical Procedure for Silver-Catalyzed Decarboxylative Chlorination of Carboxylic Acids. To a solution of adamantane-1-carboxylic acid (**A-1a**, 90 mg, 0.50 mmol) and $Ag(Phen)_2OTf$ (15.4 mg, 0.025 mmol) in anhydrous acetonitrile (5 mL) was added *tert*-butyl hypochlorite (90 μL, 0.75 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was then stirred at room temperature. After 3 h, **A-1a** was all consumed as monitored by TLC. Diluted hydrochloric acid (10 mL, 0.1 M) was then added, and the resulting mixture was extracted with dichloromethane (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10, v:v) as the eluent to give the pure product 1-chloroadamantane (**1a**) as a white solid. Mp: 164−165 °C (lit.[80] 165−166 °C). Yield: 79 mg (93%). The spectra were identical to those reported in the literature.[49]

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details, characterizations of new compounds, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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