

# Copper(I)@Carbon-Catalyzed Carboxylation of Terminal Alkynes with CO<sub>2</sub> at Atmospheric Pressure

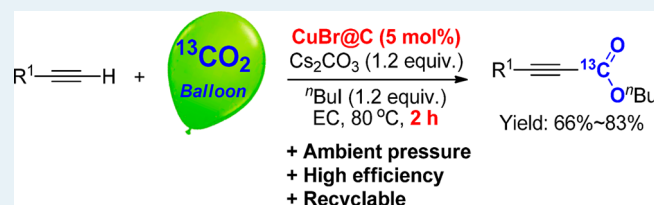
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## Supporting Information

**ABSTRACT:** Activated carbon supported CuBr was found to be an efficient catalyst for the carboxylation of terminal alkynes under atmospheric pressure of CO<sub>2</sub> using ethylene carbonate as solvent at 80 °C for only 2 h, as verified with <sup>13</sup>CO<sub>2</sub>. Various terminal alkynes could react smoothly with CO<sub>2</sub> and organic halides under the reaction conditions to afford the corresponding carboxylic esters. In addition, the catalyst can be easily recovered and reused at least five times without significant loss of activity.

**KEYWORDS:** carbon dioxide, alkynes, carboxylation, copper, heterogeneous catalysis



## INTRODUCTION

Carbon dioxide is an abundant, ubiquitous, cheap, and nontoxic gas in nature. However, the concentration of CO<sub>2</sub> in the atmosphere has risen sharply since the Industrial Revolution, primarily due to the combustion of fossil fuels.<sup>1</sup> As the principal greenhouse gas thought to be causing global warming, CO<sub>2</sub> has gained considerable attention in recent years. Consequently, a number of methods for CO<sub>2</sub> capture and storage (CCS) have been developed for mitigation of carbon emission.<sup>2–6</sup> On the other hand, catalytic transformation of CO<sub>2</sub> into value-added compounds can be regarded as a desirable alternative to CCS.<sup>7</sup>

In fact, CO<sub>2</sub> transformation on a large scale is still limited today due to its inherent thermodynamic stability and kinetic inertness. Traditionally, this challenge can be surmounted through the application of noncatalytic processes involving Grignard reagent or organolithium reagents. However, sensitive prefunctionalized substrates are required and the functional group compatibility is also questionable. Therefore, a catalytic procedure for CO<sub>2</sub> transformation under mild conditions with a broad substrate scope is highly attractive and remains a challenge.

In recent years, C–H bond functionalization has attracted much attention for the direct, concise construction of chemical bonds.<sup>8–12</sup> In particular, C–H bond carboxylation using CO<sub>2</sub> as a carboxylative reagent for C–C bond construction has emerged to synthesize carboxylic acid derivatives.<sup>13–21</sup> However, these methods generally suffer from some drawbacks: e.g. tedious reaction procedures, extended periods of time, and the formation of side products. Therefore, catalytic functionalization of C–H with CO<sub>2</sub> (ideally 1 atm of CO<sub>2</sub>) under mild

conditions with high efficiency is an important subject of research.

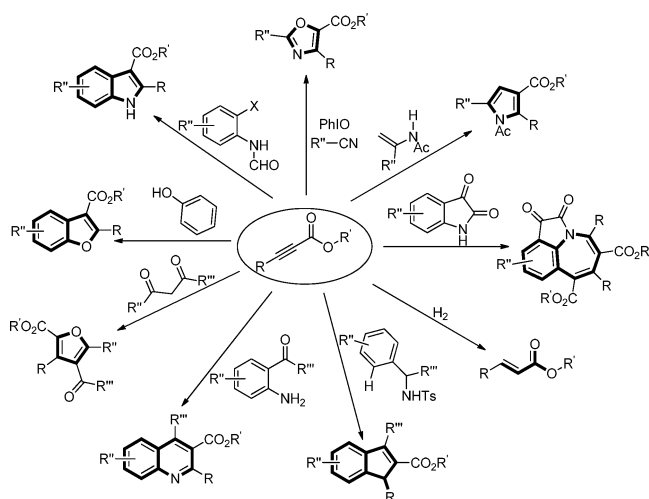
On the other hand, alkynyl carboxylic acids and their derivatives have been extensively applied in organic synthesis.<sup>22</sup> For example, alkyl 2-alkynoates have been reported as an important feedstock for the construction of heterocycles, including pyrroles,<sup>23</sup> oxazole,<sup>24</sup> indole,<sup>25</sup> oxindole,<sup>26</sup> benzofurans,<sup>27</sup> furans,<sup>28</sup> quinolines,<sup>29</sup> indene,<sup>30</sup> and benzazepines,<sup>31</sup> as depicted in Scheme 1. In this regard, several protocols have been developed to prepare carboxylic acids/esters via carboxylation of terminal alkynes with CO<sub>2</sub>,<sup>32–42</sup> which avoid the use of oxidant and toxic carbonylating reagent in the oxidative carbonylation of alkynes.<sup>43</sup>

In previous reports, a catalyst based on Cu or Ag is able to activate the triple bond of alkynes in most cases for the carboxylation with CO<sub>2</sub>. On the other hand, heterogeneous catalytic systems are favorable for industrial applications because of the ease of handling and purification of products. However, procedures employing heterogeneous catalysts have been rarely disclosed. For example, Zhang and co-workers developed a heterogeneous catalytic system for terminal alkyne carboxylation by using N-heterocyclic carbene polymer supported silver nanoparticle as an efficient catalyst.<sup>44</sup> Very recently, a zeolite-type metal–organic framework MIL-101 supported silver nanoparticle was employed for the first time as a catalyst for the coupling of CO<sub>2</sub> and terminal alkynes.<sup>45</sup> The heterogeneous catalysts showed good catalytic activity and good reusability for the carboxylation.

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## Scheme 1. Use of Alkyl 2-Alkynoates as Synthons in Organic Synthesis



In 2013, we developed a ligand-free process for the CuI-catalyzed carboxylation of terminal alkyne with ambient CO<sub>2</sub> using ethylene carbonate (EC) as solvent.<sup>46</sup> In this protocol, external ligand is avoided by using EC as solvent. However, the reusability of the transition-metal catalyst is poor under traditional conditions. Herein, we report an effective heterogeneous catalytic system using activated carbon supported CuBr for terminal alkyne carboxylation with CO<sub>2</sub> in EC under mild conditions. In addition, the catalyst is stable to air and moisture and can be easily recovered and reused.

## RESULTS AND DISCUSSION

Taking into account the high stability and easy availability of activated carbon,<sup>47–49</sup> we initiated our study by using activated carbon as a support to prepare heterogeneous copper catalysts by using the impregnation method. Different copper salts (CuX, X = Cl, Br, I) were supported on activated coconut-shell carbon (100–200 mesh), which was easily available and economically feasible (see the Supporting Information). The copper contents of CuCl@C, CuBr@C, and CuI@C, determined by graphite furnace atomic absorption spectrometry, were found to be 17.4, 12.3, and 8.3 wt %, respectively. The exploratory experiments started using phenylacetylene (**1a**) as the model substrate in the presence of *n*-BuI under atmospheric pressure of CO<sub>2</sub>. As shown in Table 1, 2 mol % of the catalyst, i.e. CuCl@C, CuBr@C, and CuI@C, was employed to promote the carboxylation under 80 °C for 15 h (entries 1–3). Among these, CuBr@C was the most efficient and delivered the desired product **2a** in 78% yield (entry 2). Control reactions established that, in the absence of any copper catalyst, base, or CO<sub>2</sub>, no satisfactory yield was observed (entry 4). Decreasing the reaction temperature to 60 °C slowed the reaction, affording a 52% yield of **2a** (entry 5). When the reaction was conducted at 100 °C, the yield of **2a** was only 33%, which was presumably due to the decarboxylation of the intermediate in the equilibrium (entry 6).<sup>33</sup> Subsequently, the reaction was investigated at 80 °C for a different period of time. However, improved yield was not observed by extending the reaction time to 24 h (entry 7). Gratifyingly, a 75% yield of **2a** was obtained even when the reaction time was reduced to 2 h (entry 8). Furthermore, an increase in the amount of CuBr@C to 5 mol % caused an increase in the yield of this reaction to

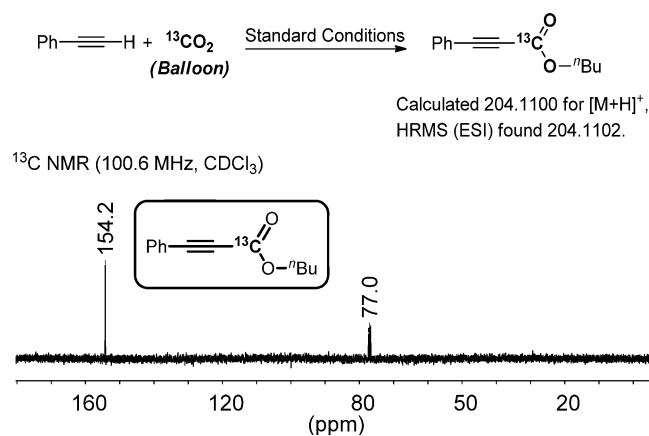
Table 1. Carboxylation of Phenylacetylene with CO<sub>2</sub><sup>a</sup>

entry	cat.	cat. loading (mol %)	T (°C)	yield (%) <sup>b</sup>
1	CuCl@C	2	80	65
2	CuBr@C	2	80	78
3	CuI@C	2	80	76
4			80	13, <sup>c</sup> 3, <sup>d</sup> 4, <sup>e</sup> 7 <sup>f</sup>
5	CuBr@C	2	60	52
6	CuBr@C	2	100	33
7 <sup>g</sup>	CuBr@C	2	80	77
8 <sup>h</sup>	CuBr@C	2	80	75
9 <sup>h</sup>	CuBr@C	5	80	90, 93 <sup>i</sup>

<sup>a</sup>Reaction conditions unless otherwise specified: phenylacetylene (51 mg, 0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (196 mg, 0.6 mmol), *n*-BuI (110 mg, 0.6 mmol), EC (3 mL), CO<sub>2</sub> (99.999%, balloon), indicated amount of catalyst (based on Cu), 15 h. <sup>b</sup>The yields were determined by GC with biphenyl as internal standard. <sup>c</sup>Without catalyst. <sup>d</sup>Without base. <sup>e</sup>Without CO<sub>2</sub>. <sup>f</sup>Equal amount of the activated carbon as a catalyst versus entry 9. <sup>g</sup>24 h. <sup>h</sup>2 h. <sup>i</sup>The recovered catalyst was used.

90% (entry 9). Interestingly, the recovered catalyst gave a 93% yield of **2a** in the second run, probably because the Cu(II) species was partially reduced under the reaction conditions, as verified by XPS measurements (vide infra).

Under the optimal conditions, the control experiment was conducted with isotopically labeled <sup>13</sup>CO<sub>2</sub> as a carboxylative reagent. As delineated in Scheme 2, the result examined by <sup>13</sup>C NMR and high resolution mass spectrometry (HRMS) confirmed that CO<sub>2</sub> was the only carboxylative reagent, rather than Cs<sub>2</sub>CO<sub>3</sub> and ethylene carbonate.

Scheme 2. Carboxylation of Terminal Alkynes with <sup>13</sup>CO<sub>2</sub> under Standard Conditions

Having established the optimal conditions, we then converted a variety of commercially available terminal alkynes into the corresponding esters to further explore the scope of this procedure under ambient CO<sub>2</sub> pressure, as summarized in Table 2. Electron rich group substituted phenylacetylenes **1b–e** (e.g., R<sup>1</sup> = 4-Me, 4-Et, 4-<sup>n</sup>C<sub>5</sub>H<sub>11</sub>, 4-MeO) were converted to the corresponding alkynoates **2b–e** in 77–81% yield (Table 2, entries 2–5). Electron-withdrawing groups substituted at the meta or ortho position (**1f–i**) were also tolerable and gave good yields (entries 6–9). The reactions with heterocyclic

Table 2. Carboxylation of Terminal Alkynes Catalyzed by CuBr@C<sup>a</sup>

$$\text{R}^1\text{-C}\equiv\text{C-H} + \text{CO}_2 \xrightarrow[\text{R}^2\text{-X (1.2 equiv.)}]{\text{CuBr@C (5 mol\%)} \text{ Cs}_2\text{CO}_3 \text{ (1.2 equiv.)}} \text{R}^1\text{-C}\equiv\text{C-C(=O)OR}^2$$

**1a-m (Balloon)**  **2a-m**

EC, 80 °C, 2 h

Entry	Alkynes	R <sup>2</sup> -X	Products	Yield (%) <sup>b</sup>
1	Ph-C≡C-H <b>1a</b>	<sup>n</sup> Bu-I	Ph-C≡C-C(=O)- <sup>n</sup> Bu <b>2a</b>	83
2	Me-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1b</b>	<sup>n</sup> Bu-I	Me-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2b</b>	80
3	Et-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1c</b>	<sup>n</sup> Bu-I	Et-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2c</b>	77
4	<sup>n</sup> C <sub>8</sub> H <sub>11</sub> -C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1d</b>	<sup>n</sup> Bu-I	<sup>n</sup> C <sub>8</sub> H <sub>11</sub> -C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2d</b>	81
5	MeO-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1e</b>	<sup>n</sup> Bu-I	MeO-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2e</b>	80
6	Cl-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1f</b>	<sup>n</sup> Bu-I	Cl-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2f</b>	77
7	F-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1g</b>	<sup>n</sup> Bu-I	F-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2g</b>	74
8	Cl-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1h</b>	<sup>n</sup> Bu-I	Cl-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2h</b>	79
9	Br-C <sub>6</sub> H <sub>4</sub> -C≡C-H <b>1i</b>	<sup>n</sup> Bu-I	Br-C <sub>6</sub> H <sub>4</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2i</b>	75
10	Thiophene-C≡C-H <b>1j</b>	<sup>n</sup> Bu-I	Thiophene-C≡C-C(=O)- <sup>n</sup> Bu <b>2j</b>	72
11	2-Pyridine-C≡C-H <b>1k</b>	<sup>n</sup> Bu-I	2-Pyridine-C≡C-C(=O)- <sup>n</sup> Bu <b>2k</b>	70
12	3-Pyridine-C≡C-H <b>1l</b>	<sup>n</sup> Bu-I	3-Pyridine-C≡C-C(=O)- <sup>n</sup> Bu <b>2l</b>	66
13	<sup>n</sup> C <sub>6</sub> H <sub>13</sub> -C≡C-H <b>1m</b>	<sup>n</sup> Bu-I	<sup>n</sup> C <sub>6</sub> H <sub>13</sub> -C≡C-C(=O)- <sup>n</sup> Bu <b>2m</b>	75
14	Ph-C≡C-H <b>1a</b>	Me-I	Ph-C≡C-C(=O)-Me <b>2n</b>	81
15	Ph-C≡C-H <b>1a</b>	Et-Br	Ph-C≡C-C(=O)-Et <b>2o</b>	78

<sup>a</sup>Standard reaction conditions: terminal alkyne (1.0 mmol), catalyst (5 mol %, based on Cu), Cs<sub>2</sub>CO<sub>3</sub> (0.3910 g, 1.2 mmol), <sup>n</sup>-BuI (0.2208 g, 1.2 mmol), ethylene carbonate (3 mL), CO<sub>2</sub> (99.999%, balloon), 80 °C, 2 h. <sup>b</sup>Isolated yield.

alkynes, such as 2-ethynylthiophene (**1j**), 2-ethynylpyridine (**1k**), and 3-ethynylpyridine (**1l**), were also practical, providing the corresponding products **2j–l** in yields of 72%, 70%, and 66%, respectively (entries 10–12). The aliphatic alkyne 1-octyne (**1m**) was also examined under the standard conditions. To our delight, the desired product was also obtained in 75% yield (entry 13). Other organic halides, including MeI and EtBr, were also employed in this procedure. As a result, reasonable yields (81% and 78%) were observed by using MeI and EtBr as alkylating reagents (entries 14 and 15).

In a final set of experiments, we further assessed the stability and reusability of the CuBr@C catalyst in the carboxylation reaction, because it is crucial to confirm that the highly active catalyst is recyclable. As is shown in Figure 1, there was no discernible loss in activity or selectivity. The results were in accordance with ICP experiments because only trace amounts of copper (87 ppb) were detected in the resultant solution collected by hot filtration after 1 h.

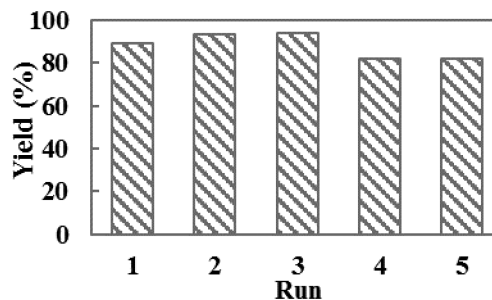
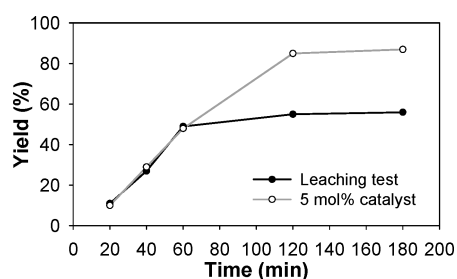


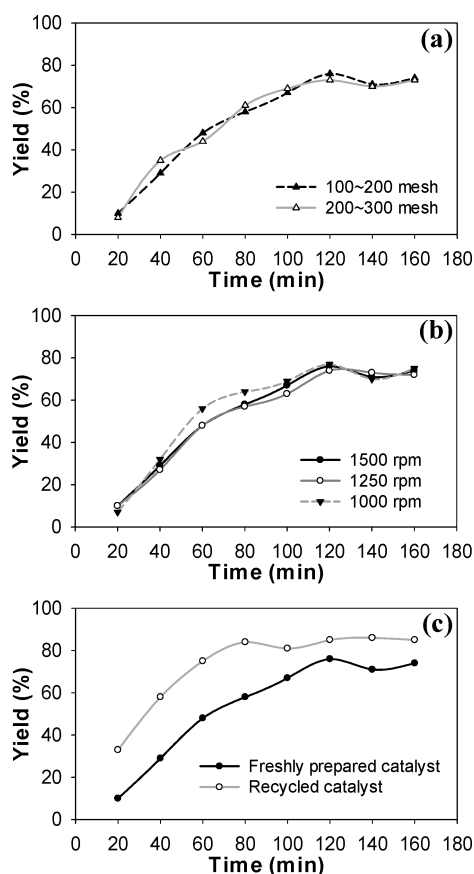
Figure 1. Recovery and reuse of CuBr@C catalyst for the carboxylation of terminal alkynes with CO<sub>2</sub>.

Moreover, the reaction with the solution after hot filtration at approximately 50% yield essentially stopped, strongly suggesting that the reaction likely proceeded on the heterogeneous surface, as illustrated in Figure 2.



**Figure 2.** Leaching test indicating no contribution from homogeneous catalysis of the active species leaching into the resultant solution.

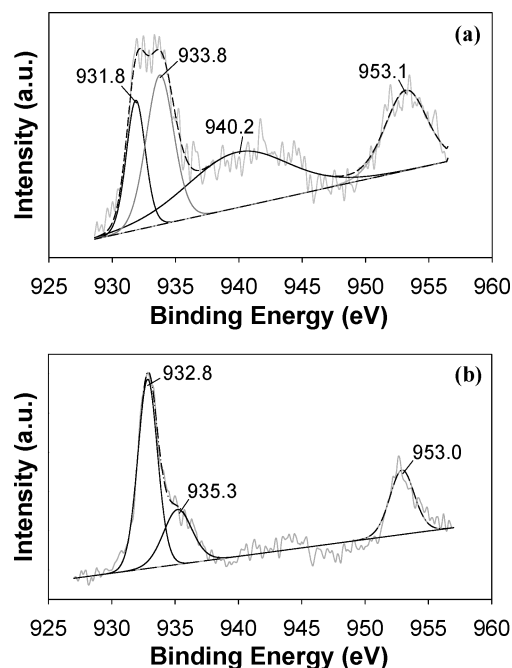
The CuBr@C catalyst before and after the reaction was characterized by Brunauer–Emmett–Teller (BET) surface area analysis and scanning electron microscopy (SEM). No significant changes were observed (see Table S1 in the Supporting Information). On the other hand, the reaction kinetics were measured as shown in Figure 3. It was observed



**Figure 3.** Reaction kinetics profile of the carboxylation reaction: (a) effects of the supporter size; (b) effects of stirring speed; (c) reaction kinetic plots by using the fresh and recovered CuBr@C catalyst, respectively. Reaction conditions unless otherwise notified: 100–200 mesh carbon as the support, 1500 rpm, 80 °C.

that similar plots were obtained for the reactions using different sizes of the activated carbon as supporter and different stirring speeds (Figure 3a,b). Surprisingly, the reaction could be slightly improved when the recovered catalyst was employed (Figure 3c). However, catalytic deactivation of the recovered catalyst appears in common heterogeneous catalysis.<sup>51</sup>

Furthermore, the electronic state of the Cu element in the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS), as shown in Figure 4.



**Figure 4.** XPS patterns of high-resolution Cu 2p of (a) as-prepared CuBr@C catalyst and (b) recovered CuBr@C catalyst.

Figure 4a shows the binding energies of Cu 2p for the CuBr@C catalyst as prepared. The distinct peaks at 933.8 and 953.1 eV are assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively. The satellite peak at 940.2 eV proves the presence of Cu(II) species, probably arising from slight oxidation of Cu<sup>+</sup> during the catalyst preparation.<sup>50</sup>

In addition, the XPS spectrum of Cu 2p for the recycled catalyst is shown in Figure 4b. Two distinct peaks at 932.8 and 953.0 eV are assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively. The very weak, in fact negligible, satellite peak means that copper mainly exists as Cu<sup>+</sup> after the carboxylative reaction. Generally, the carboxylation of terminal alkynes with CO<sub>2</sub> was catalyzed by cuprous salts rather than Cu(II).<sup>32</sup> In this case, it may be reasoned that the Cu(II) species on the surface of the catalyst were reduced to Cu<sup>+</sup> under the reaction conditions,<sup>47</sup> which may give slightly higher performance in the second and third runs.

## CONCLUSIONS

In conclusion, a CuBr@C-catalyzed carboxylation of terminal alkynes with 1 atm of CO<sub>2</sub> for the synthesis of alkyl 2-alkynoates has been developed. The readily available heterogeneous catalyst CuBr@C could be easily recovered and reused without significant loss of activity, which makes this protocol very practical and easy to handle. A range of electron-rich and electron-poor terminal alkynes could undergo the carboxylation reaction efficiently with CuBr@C as catalyst within 2 h.

## ■ ASSOCIATED CONTENT

## ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00764.

Experimental procedures, characterization data, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all products (PDF)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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