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Construction of Benzofuran-3(2*H*)-one Scaffolds with a Quaternary Center via Rh/Co Relay Catalyzed C−H Functionalization/Annulation of *N*-Aryloxyacetamides and Propiolic Acids

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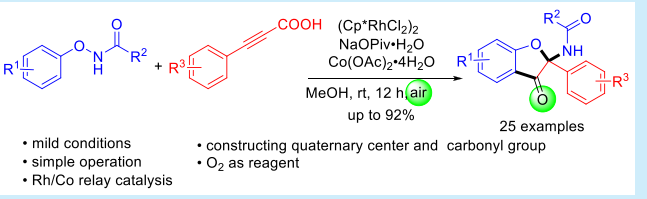
Supporting Information

ABSTRACT: An unprecedented synthesis of valuable benzofuran-3(2*H*)-one scaffolds with a quaternary center was developed via Rh/Co relay catalyzed C−H functionalization/annulation of *N*-aryloxyacetamides with propiolic acids in moderate to good yields. The reaction features the simultaneous construction of the benzofuran motif containing a C2 quaternary center and a C3 carbonyl group. The preliminary mechanism study verified that the O atom of C3 carbonyl group originates from molecular oxygen.



Benzofuran-3(2*H*)-one scaffolds, which represent one of the most important heterocycles, widely exist in natural products and bioactive molecules (Figure 1). For example,

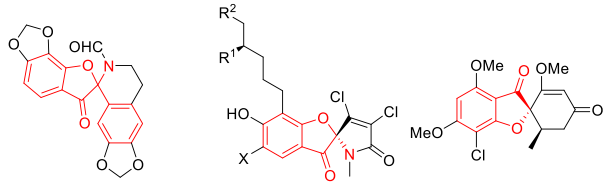


Figure 1. Selected natural products with benzofuran-3(2*H*)-one scaffolds.

coptichic aldehyde, isolated from the *Coptidis rhizoma* Euodiae, possesses cytotoxicity against human gastric carcinoma (NCI-N87) and human colon adenocarcinoma (Caco-2) cells.[1] Armeniaspiroles A−D, isolated from *Streptomyces armeniacus*, exhibit good activity against a range of multidrug-resistant Gram-positive bacterial pathogens.[2] Griseofulvin, first isolated from filamentous fungi, is the only drug available for treatment of tineacapitis caused by dermatophytes.[3] Therefore, the synthesis of benzofuran-3(2*H*)-one derivatives may be of great significance.

Transition-metal-catalyzed direct C−H functionalization has received considerable interest in recent years as a powerful and straightforward synthetic approach for complex molecules without the need for prefunctionalized substrates.[4] Among these transition-metal catalysts, Cp*Rh(III) catalysts have significantly contributed to the arsenal of heterocyclic synthesis owing to their high activity and excellent tolerance of substrate/functional group.[5] *N*-Phenoxyacetamides as the privileged substrates offer opportunities and possibilities to develop new transformations by utilizing the unique reactivity of O-NHAc acting as a redox-active directing group (DG).[6] Cp*Rh(III)-catalyzed C−H functionalization/[3 + 2] annulation of aromatic substrates bearing DG with internal alkynes to synthesize benzofuran scaffolds has been well documented.[7] Lu and co-workers reported development of a mild Rh(III)-catalyzed redox-neutral C−H functionalization of *N*-phenoxyacetamides with alkynes for the synthesis of valuable benzofuran derivatives through C−C/C−O bond formation (Scheme 1, eq 1).[8] Then they reported an efficient Rh(III)-catalyzed coupling reaction of *N*-phenoxyacetamides with propargyl carbonates to yield 3-alkylidene dihydrobenzofuran derivatives via C−H functionalization/cyclization (Scheme 1, eq 2).[9] Very recently, Zhang and co-workers reported a Rh(III)-catalyzed C−H activation of *N*-phenoxyacetamides with propiolates to afford benzofuran-2(3*H*)-ones bearing an exocyclic enamino motif with exclusive *Z* configuration selectivity via C−H functionalization/isomerization/lactonization (Scheme 1, eq 3).[10] Compared with numerous examples of constructing benzofuran scaffolds, directly constructing benzofuran-3(2*H*)-one scaffolds with a quaternary center via Rh(III)-catalyzed C−H functionalization/[3 + 2] annulation has so far remained unexplored. In continuation of our research on the development of *N*-aryloxyacetamides as a building block,[11] when *N*-aryloxyacetamides were utilized to react with propiolic acids under Rh/Co catalysis, the

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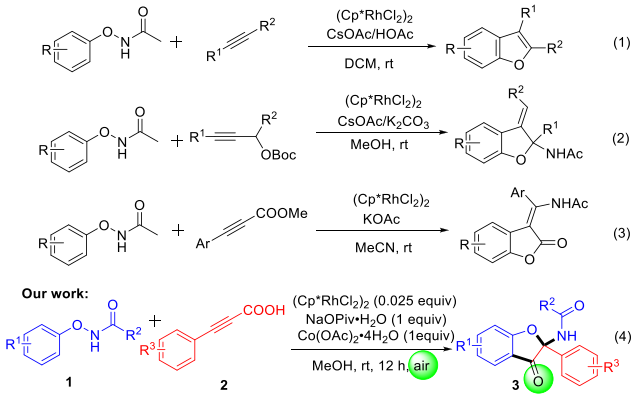
Scheme 1. Rh-Catalyzed C−H Functionalization/[3 + 2] Annulation of *N*-Aryloxyacetamides

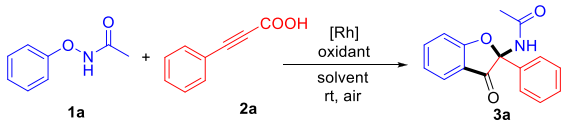


unexpected product benzofuran-3(2*H*)-one derivatives were obtained (Scheme 1, eq 4). Significantly, in this transformation, the O atom in the carbonyl group of benzofuran-3(2*H*)-one motif originates from molecular oxygen.

We commenced our investigation by examining reactions of *N*-phenoxyacetamide (**1a**) with 3-phenylpropiolic acid (**2a**) using Rh(III) catalyst [see the Supporting Information (SI)]. The reaction proceeded under an atmosphere of air, with no special precautions taken to exclude moisture. When $(Cp^*RhCl_2)_2$ (0.05 equiv) was used as the catalyst, NaOPiv·H_2O (1 equiv) as the base, $Co(OAc)_2{\cdot}4H_2O$ (1 equiv) as the oxidant, and MeOH (0.1 M) as the solvent, the desired product **3a** was obtained in 83% yield at room temperature after 12 h (Table 1, entry 1). No conversion was observed when $Co(OAc)_2{\cdot}4H_2O$ was replaced by $CoCl_2{\cdot}6H_2O$, $K_2S_2O_8$, or Oxone (Table 1, entries 2−4). $[Cp^*Rh(MeCN)_3](SbF_6)_2$ was also employed and gave **3a** in 82% yield (Table 1, entry 5). Although $(Cp^ERhCl_2)_2$ is deemed to possess higher catalytic activity than $(Cp^*RhCl_2)_2$ in the literature,[12] it provided only 78% of **3a** (Table 1, entry 6). Gratifyingly, decreasing the loading of $(Cp^*RhCl_2)_2$ to 0.025 equiv could give 92% yield of **3a** (Table 1, entry 7). However, further decreasing the loading of$(Cp^*RhCl_2)_2$ to 0.0125 equiv showed a reduction in 82% yield (Table 1, entry 8). Screening of other solvents such as DCE, HFIP, and *t*-AmylOH showed that MeOH was the best solvent in this transformation (Table 1, entries 9−11). Control experiments revealed that **3a** could not be obtained in the absence of $(Cp^*RhCl_2)_2$ and $Co(OAc)_2{\cdot}4H_2O$ (Table 1, entries 12 and 13). Therefore, the optimal reaction conditions were determined as $(Cp^*RhCl_2)_2$ (0.025 equiv), NaOPiv·H_2O (1 equiv), and $Co(OAc)_2{\cdot}4H_2O$ (1 equiv) in MeOH at room temperature for 12 h.

After establishing the optimal reaction conditions, we investigated the substrate scope using various *N*-phenoxyacetamides **1** and propiolic acids **2**. As shown in Scheme 2, *para*-substituted *N*-phenoxyacetamides with electron-withdrawing groups such as halogens and CF_3 delivered the desired benzofuran-3(2*H*)-one derivatives in moderate to good yields (**3b−e**). However, *N*-(3,5-dichlorophenoxy)acetamide did not provide the corresponding product **3f**, which might be due to the steric hindrance of Cl. Similar results could be obtained for *N*-phenoxyacetamides bearing electron-donating groups (**3g−k**). To our delight, when a long-chain *N*-phenoxyamide such as *n*-Bu was applied in the reaction, the corresponding product **3l** could be isolated in yield of 81%. Next, a variety of propiolic acids **2** were utilized, and the results showed the propiolic acids

Table 1. Optimization of Reaction Conditions for 3a[a]



entry	catalyst (equiv)	oxidant	solvent	yield[b] (%)
1	$(Cp^*RhCl_2)_2$ (0.05)	$Co(OAc)_2{\cdot}4H_2O$	MeOH	83
2	$(Cp^*RhCl_2)_2$ (0.05)	$CoCl_2{\cdot}6H_2O$	MeOH	NR
3	$(Cp^*RhCl_2)_2$ (0.05)	$K_2S_2O_8$	MeOH	NR
4	$(Cp^*RhCl_2)_2$ (0.05)	Oxone	MeOH	NR
5	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (0.05)	$Co(OAc)_2{\cdot}4H_2O$	MeOH	82
6	$(Cp^ERhCl_2)_2$ (0.05)	$Co(OAc)_2{\cdot}4H_2O$	MeOH	78
7	**$(Cp^*RhCl_2)_2$ (0.025)**	**$Co(OAc)_2{\cdot}4H_2O$**	**MeOH**	**92**
8	$(Cp^*RhCl_2)_2$ (0.0125)	$Co(OAc)_2{\cdot}4H_2O$	MeOH	82
9	$(Cp^*RhCl_2)_2$ (0.025)	$Co(OAc)_2{\cdot}4H_2O$	DCE	78
10	$(Cp^*RhCl_2)_2$ (0.025)	$Co(OAc)_2{\cdot}4H_2O$	HFIP	73
11	$(Cp^*RhCl_2)_2$ (0.025)	$Co(OAc)_2{\cdot}4H_2O$	*t*-AmylOH	87
12		$Co(OAc)_2{\cdot}4H_2O$	MeOH	NR
13	$(Cp^*RhCl_2)_2$ (0.05)		MeOH	NP

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.25 mmol), NaOPiv·H_2O (1 equiv), oxidant (1 equiv), solvent (2 mL), rt, under air, 12 h. [b]Isolated yields. NR = no reaction, NP = no product. Cp* = pentamethylcyclopentadienyl, Cp^E = 1,3-bis(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, *t*-AmylOH = 2-methyl-2-butanol.

bearing both electron-withdrawing and electron-donating substituents at different positions could react smoothly with **1a** to afford the corresponding benzofuran-3(2*H*)-ones in good to excellent yields (**3m−z**).

Interestingly, a benzofuran-3-carboxylic acid product **4** (confirmed by X-ray single-crystal diffraction, see the SI) was obtained in moderate yield when 3-(2-methoxyphenyl)-propiolic acid (**2o**) and pent-2-ynoic acid (**2p**) were applied in this reaction under the optimized conditions (Scheme 3).

In order to demonstrate the synthetic utility of this method, the model reaction was performed on a 5 mmol scale under the standard conditions, and the desired product **3a** was provided in 76% yield (Scheme 4).

To obtain a better understanding of the reaction mechanism, a series of control experiments were carried out. Two radical-trapping experiments were conducted with 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) as radical scavengers. The results showed the reactions were inhibited, which supports a radical pathway (Scheme 5, eq 1). To probe the active intermediate, a stable five-membered rhodacycle complex **A** was prepared.[6b,m] Significantly, only 1 mol % of **A** could catalyze effectively the model reaction to give **3a** in 75% yield. The reaction of a stoichiometric rhodacycle **A** with **2a** facilely conversed into **3a** in 95% yield. These results suggest that rhodacycle **A** was involved in the catalytic cycle as the active species (Scheme 5, eqs 2 and 3). Since this cyclization process includes a C−H activation step, a kinetic isotopic effect (KIE) of 2.5 was observed in a competitive experiment. Another, a KIE of 1.6,

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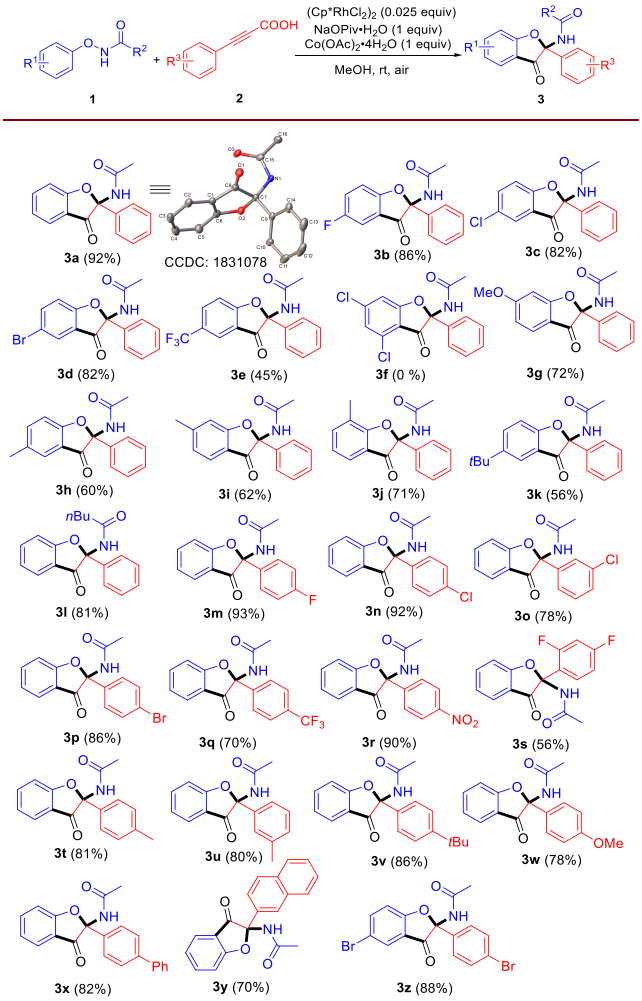
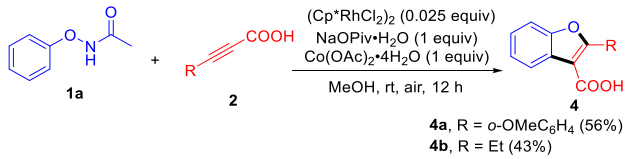
Scheme 2. Synthesis of Benzofuran-3(2*H*)-ones[a,b]



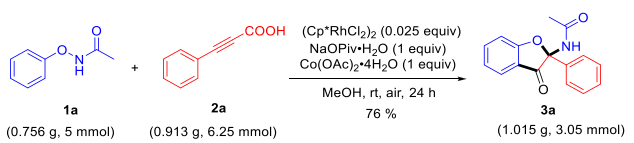
[a]Reaction conditions: **1** (0.20 mmol), **2** (0.25 mmol), $(Cp^*RhCl_2)_2$ (0.025 equiv), NaOPiv·H_2O (1 equiv), $Co(OAc)_2{\cdot}4H_2O$ (1 equiv), MeOH (2 mL), rt, 12 h. [b]Isolated yields.

Scheme 3. Synthesis of Benzofuran-3-carboxylic Acid[a,b]



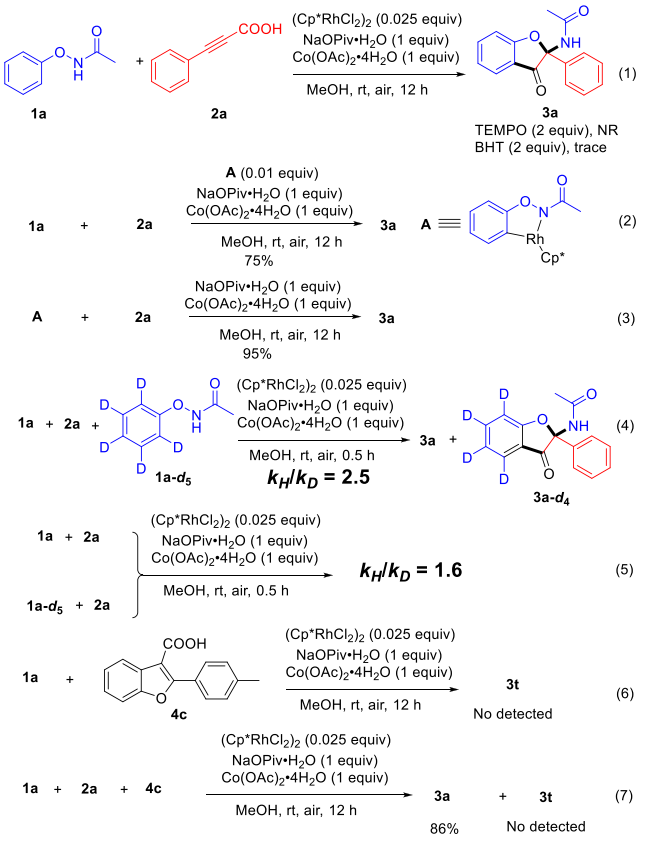
[a]Reaction conditions: **1a** (0.20 mmol), **2** (0.25 mmol). [b]Isolated yield.

Scheme 4. Gram-Scale Experiment



was observed from two side-by-side reactions using **1a** and **1a**-d_5. These results suggest that C−H bond cleavage occurs in the rate-determining step (Scheme 5, eqs 4 and 5). Finally, to demonstrate whether benzofuran-3-carboxylic acids **4** are an intermediate in this transformation, 2-(*p*-tolyl)benzofuran-3-

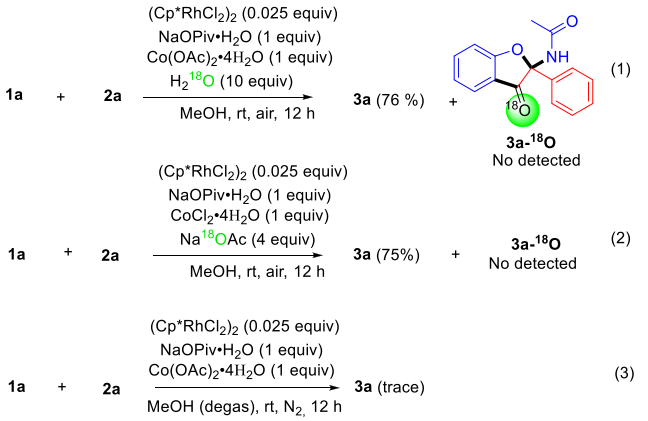
Scheme 5. Control Experiments



carboxylic acid (**4c**) was prepared to react with **1a**. However, **3t** was not detected. Considering that **2** may play an important role in this conversion reaction, the three-component reaction of **1a**, **2a** ,and **4c** was conducted. Unfortunately, only **3a** was detected, but **3t** still could not be obtained (Scheme 5, eqs 6 and 7) (see the SI). The results suggest the benzofuran-3-carboxylic acid could not be an intermediate in the reaction.

Isotopic labeling experiments were conducted to further elucidate the source of the O atom of the benzofuran-3(2*H*)-one C3 carbonyl group (Scheme 6). First, two labeled reagents, $H_2{}^{18}O$ and $Na^{18}OAc$, were applied in the reaction, and **3a**-^{18}**O** was not detected by HRMS (Scheme 6, eqs 1 and 2). Next, the reaction of **1a** with **2a** was carried out in degassed MeOH at rt in the glovebox, only trace **3a** was obtained

Scheme 6. Isotopic Labeling Experiments



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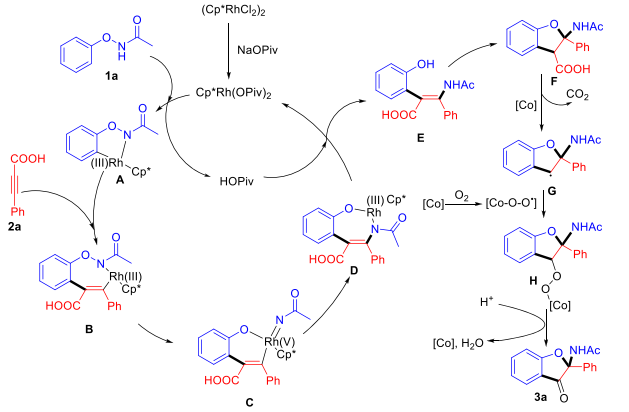
(Scheme 6, eq 3) (see the SI). These results suggest that O_2 is the exclusive source of the O atom in the carbonyl group of benzofuran-3(2*H*)-one scaffolds.

To probe the role of $Co(OAc)_2{\cdot}4H_2O$ in the catalytic cycle, the solutions of two control reactions were analyzed by LC−MS. (1) The model reaction was carried out for 1 h under the standard conditions, and the intermediates **E** and **3a** were detected (**E** $[M - H]^-$ 296.07; **3a** $[M + H]^+$ 268.06. (2) The model reaction without added $Co(OAc)_2{\cdot}4H_2O$ was carried out for 1 h, and the intermediate **E** was still detected but **3a** could not be detected. Then $Co(OAc)_2{\cdot}4H_2O$ was added into the reaction system for 20 min, and **3a** was obtained in 13% yield (see the SI). The results suggest $Co(OAc)_2{\cdot}4H_2O$ could play a key role in decarboxylation/cyclization.

On the basis of the above observations, a tentative mechanism for the reaction of **1a** with **2a** to afford the product **3a** is depicted in Scheme 7. First, the coordination of

Scheme 7. Possible Mechanism for the Transformation



1a to the catalytically active species $Cp^*Rh(OPiv)_2$ from $(Cp^*RhCl_2)_2$ and NaOPiv gives the rhodacycle complex **A**. Next, an alkyne insertion of **2a** to **A** provides intermediate **B**. An intramolecular oxidative addition of Rh(III) to the N−O bond gives the six-membered Rh(V) nitrenoid intermediate **C**.[6c,d] Subsequent intramolecular nitrenoid migration produces a seven-membered Rh(III) intermediate **D**. Then the protodemetalation of **D** provides the intermediate **E** along with the active catalyst $Cp^*Rh(OPiv)_2$. The cyclization of intermediate **E** provides **F**, which undergoes a [Co]-mediated decarboxylation to generate the radical **G**. The radical **G** traps the $[Co-O-O^\bullet]$ species generated from [Co] under air[13] to form hydroperoxide species **H**, and **H** eventually provides the desired product **3a**.

In summary, we have developed an unprecedented Rh/Co relay catalyzed [3 + 2] C−H functionalization/annulation for the construction of benzofuran-3(2*H*)-one scaffolds with a quaternary center from *N*-aryloxyacetamides and propiolic acids. The reaction features simultaneous construction of a benzofuran motif containing a C2 quaternary center and a C3 carbonyl group. The O atom of the C3 carbonyl group originates from molecular oxygen. Considering the simple operation, large-scale preparation, and valuable benzofuran-3(2*H*)-one scaffolds, this synthetic strategy should have potential synthetic utility in natural products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00181.

Experimental procedures, characterization and spectral data (PDF)

Accession Codes

Accession Codes CCDC 1831078, 1855373 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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