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Markovnikov-Selective Hydroboration of Olefins Catalyzed by a Copper N‑Heterocyclic Carbene Complex

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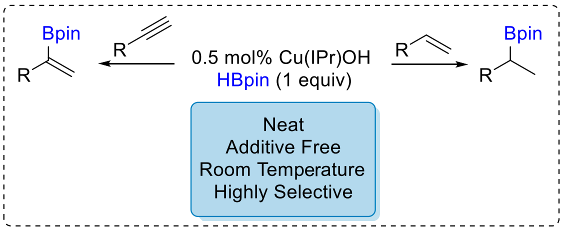
Supporting Information

ABSTRACT: The efficient and atom-economical hydroboration of alkenes and alkynes using an N-heterocyclic carbene (NHC) copper hydroxide catalyst has been developed. An equimolar combination of substrate and HBpin allows for the selective Markovnikov hydroboration of alkenes and alkynes. A variety of functional groups were tolerated in good to excellent yield. This system features a facile reaction setup, atom economy, high selectivity, and an easily synthesized copper−NHC catalyst.



■ INTRODUCTION

Organoboron compounds are highly valuable synthetic intermediates used in a variety of organic transformations.[1] Mainly, the synthetic utility of the boronate group has been illustrated in many Suzuki−Miyaura coupling reactions to form C−C bonds.[2] Classically, organoboron compounds are synthesized via Grignard or organolithium reagents.[3] Alternatively, the use of a transition-metal catalyst is an attractive strategy to access the organoboron motif.[4] Whereas many catalytic advances have been made toward the synthesis of organoboron compounds, selectivity and atom economy still remain a challenge.

Over the years, many examples of first-row metal-containing catalysts in conjunction with supporting ligands have been reported for hydroboration reactions.[5−12] Notably, N-heterocyclic carbenes (NHCs) have attracted attention as tunable ligands for catalysis.[13] Recently, copper−NHC complexes have been prevalent in the literature for transforming alkenes and alkynes to their borylated counterparts. Using a combination of a simple copper salt, an NHC, and a base, Hoveyda reported the hydroboration of aryl-substituted alkenes[14] and acyclic and exocyclic 1,1-disubstituted aryl alkenes.[15] More recently, Whittlesey reported the use of (NHC)Cu(O^{t}Bu) complexes for the hydroboration of alkynes; however, the scope was limited to internal alkynes.[16] Nickel and iron NHC complexes have also been developed for the hydroboration of styrene and vinyl arenes. In 2016, Schomaker developed a heteroleptic nickel NHC complex for the Markovnikov-selective hydroboration of styrenes.[17] That same year, Thomas developed a switchable Markovnikov/anti-Markovnikov system catalyzed by an alkoxy-tethered NHC iron complex.[18] Despite the many catalytic strategies that have been developed for selective Markovnikov or anti-Markovnikov products, most systems still form some amount of the undesired product.

Herein we report a Markovnikov-selective hydroboration of alkenes and alkynes catalyzed by a transition-metal base Cu(IPr)(OH) **1** (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). A variety of functional groups are tolerated, giving products in good to excellent yield. The use of equimolar amounts of borylating agent and substrate allow for the facile transformation to the organoborane at room temperature. Furthermore, low catalyst loading, neat conditions, and atom economy provide for an efficient and low-cost method for obtaining valuable organoboranes.

■ RESULTS AND DISCUSSION

We began our study by investigating the hydroboration of styrene **2a** catalyzed by copper hydroxide Cu(IPr)(OH) **1**. Initial screens exclusively yielded the Markovnikov product, albeit in low yield. A drastic increase in the yield of **3a** was observed when the reaction was carried out under more concentrated conditions (Table 1, entries 1 and 2). Running the reaction neat allowed for the efficient conversion of **2a** to **3a** in high yield while conserving the Markovnikov selectivity (entry 3). In an effort to develop an efficient, atom-economical, and cost-effective transformation, lower catalyst loadings were explored. Lower catalyst loadings were tolerated (entries 4 and 5), but upon decreasing the loading to 0.25 mol %, the reaction did not go to completion after 24 h. Control reactions showed that catalyst is necessary for this transformation, whereas the addition of solvent is not (entries 6 and 7). For this system, 0.5 mol % catalyst loading and neat conditions proved to be optimal for the hydroboration of **2a** to **3a** (entry 4).

With the optimized reaction conditions in hand, various alkenes and alkynes were tested (Table 2). In general, substrates bearing para-electron withdrawing groups are well tolerated (Table 2, **3b−e**). In the case of **3b** and **3d**, increasing the catalyst loading to 1.0 mol % allowed for a higher conversion to the borylated product. For substrates with electron-donating substituents, borylation proved to be more challenging. Compared with a substrate with a mild electron-

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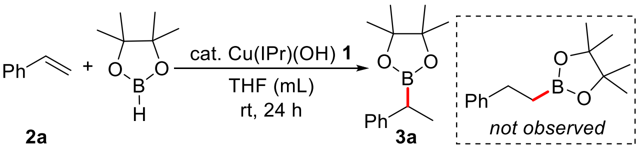
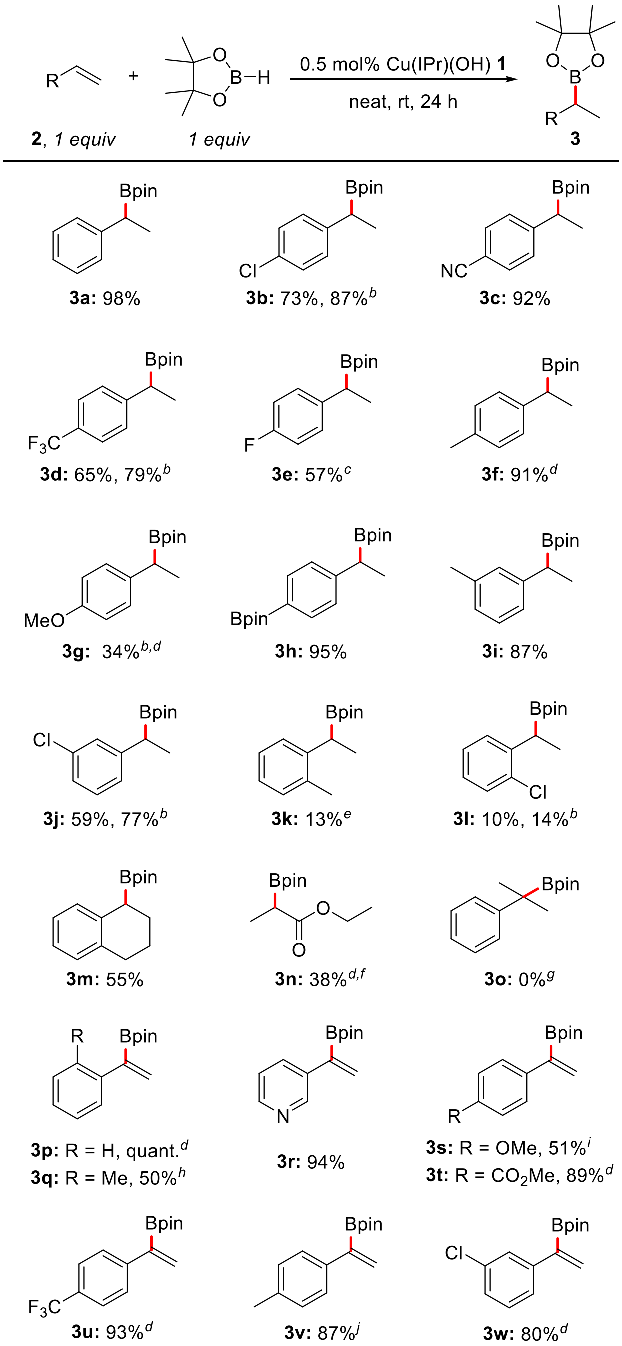
Table 1. Optimization of Standard Reaction Conditions[a]



entry	cat. loading	THF (mL)	yield **3a** (%)[b]
1	1.0 mol %	1.0	18
2	1.0 mol %	0.5	39
3	1.0 mol %		96
4	0.50 mol %		98
5	0.25 mol %		80
6			0
7		0.5	0

[a] Reaction conditions: alkene (0.5 mmol), HBpin (0.5 mmol), catalyst, THF (mL), rt, 24 h (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). [b] Yield determined via ^{1}H NMR spectroscopy versus 2,4,6-trimethylbenzaldehyde as an internal standard.

Table 2. Hydroboration Substrate Scope[a]

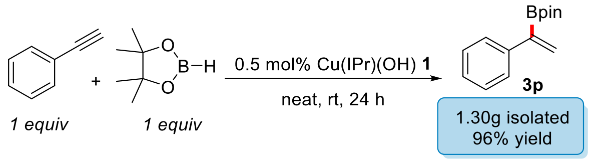


[a] Yield determined via ^{1}H NMR spectroscopy versus 2,4,6-trimethylbenzaldehyde as an internal standard (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). [b] 1.0 mol % catalyst loading. [c] Yield determined via ^{19}F NMR spectroscopy versus 4-fluorobenzoic acid as an internal standard. [d] Trace amount of linear product observed by GC−MS (<1%); not observed by ^{1}H NMR spectroscopy. [e] Isolated yield. [f] α,α,α-Trifluorotoluene used as the internal standard. [g] Branched product observed by GC−MS (<5%). [h] 43% of the linear product observed by ^{1}H NMR spectroscopy. [i] 4% of linear product observed by ^{1}H NMR spectroscopy. [j] 8% of linear product observed by ^{1}H NMR spectroscopy.

donating group (**3f**), a substrate with a strong electron-donating group in the para position (**3g**) significantly decreased the yield, even at a higher catalyst loading. Attempts to further optimize the reaction conditions for **3g** did not drastically improve the conversion, indicating that substrates with strong electron-donating groups are not well-tolerated with this system.[19] Next, substrates featuring ortho and meta functionality were examined. *meta*-Methyl substitution (**3i**) results in a slight decrease in yield (compared with **3f**), whereas ortho substitution (**3k**) gave poor conversion and poor yield, attributable to steric hindrance. Increasing the catalyst loading to 1.0 mol % did result in an increase in yield for the meta-substituted derivative **3j**; however, this was not the case for ortho-substituted derivative **3l**. Furthermore, the scope of the reaction was extended to internal alkene **3m** and acrylate substrate **3n**. Strikingly, no linear borylation product of α-methylstyrene (**3o**) was observed, highlighting the selectivity of this system for Markovnikov product.

Borylation of alkynes proceeded in a modest to high yield, 46−99% yield (Table 2, **3p**−**w**). Unlike **3k**, the borylation of *ortho*-methyl-substituted alkyne **3q** proceeded in high conversion (93%), suggesting that steric hindrance is not detrimental for the borylation of alkynes. However, *ortho*-methyl substitution results in the loss of Markovnikov selectivity, yielding a ∼1:1 ratio of the branched and linear products. Unlike **3j**, the borylation of *meta*-chloro-substituted alkyne **3w** proceeded in high conversion (80%) under standard conditions. Methyl 4-vinylbenzoate was also tested, and the corresponding borylated product **3t** was obtained in high yield, 89%. Strongly donating *para*-methoxy-substituted alkyne **3s** was tolerated in modest yield. This was not the case for *para*-methoxy-substituted alkene, **3g**. Mildly donating *para*-methyl-substituted alkyne converted to product **3v** in high yield (87%), mirroring the reactivity of alkene **3f** (91%). Strongly withdrawing trifluoromethyl-substituted alkyne **3u** proceeded in high yield (93%). The scope of the reaction was extended to 3-ethynylpyridine, and the corresponding product **3r** was obtained in high yield. Lastly, the practicality of this transformation was illustrated by accessing **3p** on a gram scale (eq 1).

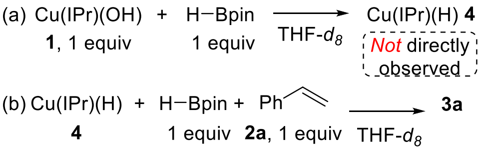
Moving forward, we sought to explore the mechanism of the reaction. NHC ligands have been reported to stabilize low-coordinate, reactive copper(I) complexes.[20,21] In 2004, Sadighi reported that the reaction of $\mathrm{Cu(IPr)(O^tBu)}$ with triethoxysilane in C_6D_6 generates a dimeric copper(I) hydride complex.[20] This complex is unstable at room temperature and will start to decompose within 1 h to give Cu^0 precipitate.



(1)

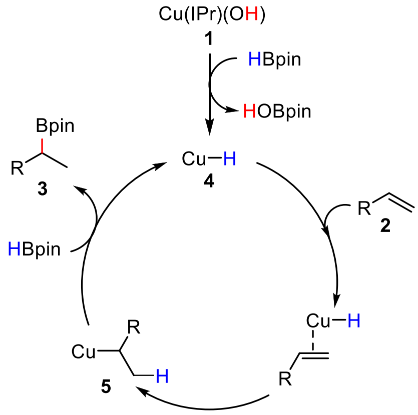
Given these results, we sought to examine the in situ stoichiometric formation of Cu(IPr)(H) **4** in benzene-d_6 (Scheme 1a). Indeed, the reaction of **1** with HBpin results in a rapid reaction with the immediate appearance of an intense yellow color.[22] This observation is consistent with the color change observed in the previously mentioned formation of a copper(I) hydride complex in C_6D_6.[20] Furthermore, in tetrahydrofuran-d_8, the ^1H NMR spectrum of **1** shows the characteristic broad singlet of the OH group at δ −1.91. Upon the addition of HBpin, the resonance at δ −1.91 disappears, likely due to the formation of a copper hydride, which is well precedented in the literature.[23,24] The addition of **2a** and HBpin to a solution containing the proposed intermediate (Scheme 1b) indeed yields borylated product **3a**, suggesting that the copper species formed is an on-cycle active catalytic intermediate. (See the Supporting Information for more details.)

Scheme 1. Stoichiometric Experiments



With the insight gained from these mechanistic experiments along with literature precedent,[20,23,24] a plausible mechanism is proposed (Scheme 2). The reaction of complex **1** with HBpin generates the active catalyst **4**, a Cu(I)−hydride complex. Coordination of the alkene, followed by migratory insertion gives species **5**. Reaction of **5** with HBpin affords borylated product **3**, regenerating the active catalyst **4**. The high regiochemistry obtained can be attributed to the strong preference for the branched isomer **5**. This preference can be attributed to the formation of the strong methyl β-C−H bond in **5**, as the metal−benzylic carbon bond is expected to be weak.[25]

Scheme 2. Proposed Catalytic Cycle



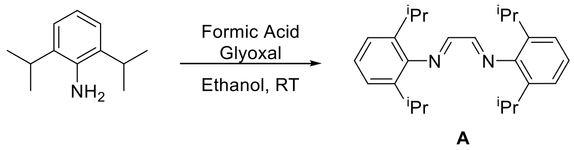
CONCLUSIONS

We have successfully developed the highly Markovnikov-selective copper(I)-catalyzed hydroboration of alkenes and alkynes. It was found that substrates with electron-withdrawing groups are well-tolerated, whereas substrates with strong electron-donating groups hinder reactivity. Furthermore, steric hindrance plays an important role, with ortho substitution of the styrene being detrimental for catalysis. The electronic and steric effects are less important for the hydroboration of alkynes. The current strategy features high selectivity for the Markovnikov product, excellent atom economy, low catalyst loading, and neat reaction conditions making this an attractive strategy for the hydroboration of alkenes and alkynes.

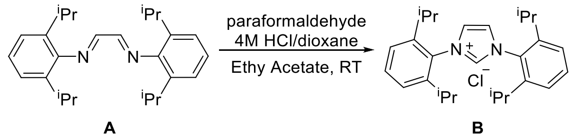
EXPERIMENTAL SECTION

General. Unless otherwise noted, all organometallic compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and glovebox techniques. (1*E*,2*E*)-N^1,N^2-Bis(2,6-diisopropylphenyl)-ethane-1,2-diimine **A** was synthesized according to the literature procedure.[26] 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene **B** was synthesized according to the literature procedure.[27] Compound **C** (Cu(IPr)Cl) was synthesized according to the literature procedure[28] and purified according to the literature procedure.[29] Compound **1** (Cu(IPr)(OH)) was synthesized according to the literature procedure.[30]

*Synthesis of (1E,2E)-N^1,N^2-Bis(2,6-diisopropylphenyl)-ethane-1,2-diimine (**A**).* A 500 mL round-bottomed flask containing a stir bar was charged with 2,6-diisopropylaniline (280 mmol, 1.00 equiv), glyoxal (140 mmol, 0.500 equiv), 100% anhydrous ethanol (250 mL), and two drops of formic acid. The reaction was stirred at room temperature for 48 h. A yellow precipitate started to form after 4 h. After 48 h, the reaction was gravity filtered. The yellow precipitate was washed with cold methanol and dried on a vacuum line to afford **A** (33.8 g, 64% yield). Compound **A** was used in the next step without further purification. Spectroscopic data match the reported data.[26] ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 2 H), 7.22−7.14 (m, 6 H), 3.00−2.88 (m, 4 H), 1.21 (d, *J* = 6.8 Hz, 24 H).

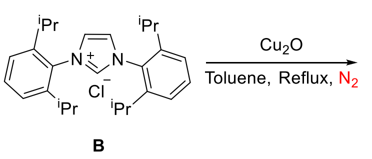


*Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (**B**).* A 50 mL round-bottomed flask containing a stir bar was charged with paraformaldehyde (46.0 mmol, 1.10 equiv) and 4 M HCl/dioxane solution (63.0 mmol, 1.50 equiv). The reaction was stirred until most of the paraformaldehyde dissolved. A 250 mL three-necked round-bottomed flask equipped with an addition funnel and stir bar was charged with **A** (42.0 mmol, 1.00 equiv) and ethyl acetate (85.0 mL). The paraformaldehyde solution was then added to the addition funnel and added dropwise over the course of 1 h. The addition of the paraformaldehyde solution caused the yellow solution containing **A** to turn orange. A white precipitate formed after 5 min. After the slow addition was complete, the solution was orange/brown with an additional white precipitate. The reaction was stirred at room temperature for 16 h, at which point the precipitate was brown/orange. The brown/orange solid was gravity filtered and washed with ethyl acetate, affording a light-pink solid. The light-pink solid was dissolved in chloroform and then concentrated in vacuo and dried on

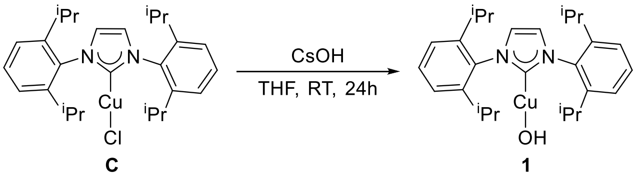


a vacuum line to afford **B** (21.4 g, 86% yield). Spectroscopic data match the reported data.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1 H), 8.15 (s, 2 H), 7.58 (t, J = 7.8 Hz, 2 H), 7.35 (d, J = 7.8 Hz, 4 H), 2.51−2.40 (sept, J = 6.8, 4 H), 1.29 (d, J = 6.8 Hz, 12 H), 1.25 (d, J = 6.9 Hz, 12 H).

*Synthesis of Cu(IPr)Cl (**C**).* An oven-dried 250 mL round-bottomed flask equipped with a stir bar was charged with **B** (9.36 mmol, 1.54 equiv) and Cu_2O (6.08 mmol, 1 equiv). The flask was then fitted with a reflux condenser capped with a septum, and the system was put under a nitrogen atmosphere. The system was then charged with toluene (40 mL) and refluxed for 4 days. The reaction was then cooled, and CH_2Cl_2 was added to dissolve any solid that had formed. The reaction was transferred to a separatory funnel and washed with water (2 × 100 mL) to remove any unreacted imidazolium salt. The organic layer was dried over sodium sulfate and concentrated in vacuo. The resulting dark-brown solid was transferred to a frit and washed with pentane. The solid turned from dark-brown to light-purple. The light-purple solid was recrystallized by dissolving the product in CH_2Cl_2, stirring over K_2CO_3, and gravity filtering to remove the K_2CO_3. The product was then precipitated by the slow addition of pentane through an addition funnel. The solid was gravity filtered and dried on a vacuum line to afford **C** (1.4 g, 31% yield). Spectroscopic data match the reported data.[32] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, J = 7.8 Hz, 2 H), 7.30 (d, J = 7.8 Hz, 4 H), 7.13 (s, 2 H), 2.63−2.50 (sept, J = 6.8 Hz, 4 H), 1.30 (d, J = 6.9 Hz, 12 H), 1.23 (d, J = 6.9 Hz, 12 H). Elemental analysis calculated for $C_{27}H_{36}N_2CuCl$ (MW 487.59 g/mol): C, 66.51; H, 7.44; N, 5.75. Found: C, 66.59; H, 7.49; N, 5.53. **Note:** The final product varies in color from pale-purple to off-white. Sometimes multiple recrystallizations are required to get a pure product. The purity of **C** greatly affects the yield of **1**.



*Synthesis of Cu(IPr)(OH) (**1**).* An oven-dried 150 mL round-bottomed flask was charged with **C** (2.50 mmol, 1.00 equiv), CsOH (5.00 mmol, 2.00 equiv), and THF (48.0 mL). The reaction solution, pale-orange in color, was allowed to stir at room temperature for 24 h. The reaction was then filtered through a celite plug into a Schlenk flask and concentrated in vacuo until three-fourths of the solvent was removed. Pentane was then added to precipitate the product. The product was then isolated by filtration onto a glass frit and washed with pentane. The resulting white solid was dried on a vacuum line to afford **1** (0.985 g, 84%). Spectroscopic data match the reported data.[33] Note that we do not see a resolution between the literature-reported triplet at δ 7.46 and the singlet at δ 7.43. We observe a multiplet that integrates to 4 H. The literature does not report the OH shift in the NMR spectrum, but we are able to observe a broad singlet OH shift at δ −1.91. ^{1}H NMR (500 MHz, THF): δ 7.45 (m, 4 H), 7.32 (d, J = 7.6 Hz, 4 H), 2.65 (m, 4 H), 1.31 (d, J = 6.6 Hz, 12 H), 1.21 (d, J = 6.7 Hz, 12 H), −1.91 (s, 1 H). Elemental analysis calculated for $C_{27}H_{37}CuN_2O$ (MW 469.14): C, 69.12; H, 7.95; N, 5.97. Found: C, 68.98; H, 7.74; N, 5.78.



General Procedure for Hydroboration. In a glovebox, an oven-dried 1-dram vial containing a stir bar was charged with Cu(IPr)(OH) (0.50 mol %, 0.05 equiv), styrene **2** (0.50 mmol, 1.0 equiv), and HBpin (0.50 mmol, 1.0 equiv). The reaction was capped and removed from the glovebox and stirred at room temperature for 24 h. The reaction was then filtered through a celite plug. The 1-dram vial was washed with CH_2Cl_2 (5 × 0.5 mL), and the washings were filtered through the plug. The combined washings were concentrated in vacuo and analyzed by ^{1}H NMR spectroscopy utilizing 1,4,6-trimethylbenzaldehyde as the internal standard. **Note**: In conjunction with NMR analysis, the reaction was also analyzed using GC−MS. The GC−MS trace showed no formation of the linear product, which comes at a distinctly different retention time than the branched product. See the Supporting Information. **Note**: Although reaction conditions are neat, substrates that are solids are still able to be borylated (**2h**, **2r**, **2t**). **Note**: The neat large-scale reaction is extremely exothermic. The slow addition of HBpin is recommended.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00394.

> Details of the optimization of the borylation reaction, NMR spectra of stoichiometric reactions, and product characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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