CoIII−Carbene Radical Approach to Substituted 1H-Indenes

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Supporting Information

ABSTRACT: A new strategy for the catalytic synthesis of substituted 1H-indenes via metalloradical activation of o-cinnamyl N-tosyl hydrazones is presented, taking advantage of the intrinsic reactivity of a CoIII carbene radical intermediate. The reaction uses readily available starting materials and is operationally simple, thus representing a practical method for the construction of functionalized 1H-indene derivatives. The cheap and easy to prepare low spin cobalt(II) complex [CoII(MeTAA)] (MeTAA = tetramethyltetraaza[14]annulene) proved to be the most active catalyst among those investigated, which demonstrates catalytic carbene radical reactivity for a nonporphyrin cobalt(II) complex, and for the first time catalytic activity of [CoII(MeTAA)] in general. The methodology has been successfully applied to a broad range of substrates, producing 1H-indenes in good to excellent yields. The metallo-radical catalyzed indene synthesis in this paper represents a unique example of a net (formal) intramolecular carbene insertion reaction into a vinylic C(sp2)−H bond, made possible by a controlled radical ring-closure process of the carbene radical intermediate involved. The mechanism was investigated computationally, and the results were confirmed by a series of supporting experimental reactions. Density functional theory calculations reveal a stepwise process involving activation of the diazo compound leading to formation of a CoIII-carbene radical, followed by radical ring-closure to produce an indanyl/benzyl radical intermediate. Subsequent indene product elimination involving a 1,2-hydrogen transfer step regenerates the catalyst. Trapping experiments using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical or dibenzoylperoxide (DBPO) confirm the involvement of cobalt(III) carbene radical intermediates. Electron paramagnetic resonance spectroscopic spin-trapping experiments using phenyl N-tert-butylnitrone (PBN) reveal the radical nature of the reaction.

INTRODUCTION

Substituted indenes and their closely related indane derivatives are important structural motifs found in many natural products such as taiwaniaquinol,1 cyanosporaside A/B,2 biological active molecules such as endothelin receptors antagonist enrasentan,3 an antipruritic dimetindene,4 melatonin receptor,5 anti-inflammatory sulindac,6 aldosterone synthase inhibitors,7 and antitubercular agents.8 Some of them are market-leading drugs and/or key intermediates for the synthesis of natural products, pharmaceuticals and other bioactive compounds, as well as functional materials9 and metallocene complexes for olefin polymerization (Figure 1).10 Because of their importance and usefulness, construction of the indene skeleton has attracted interest of synthetic organic and medicinal chemists for several years. Several synthetic methodologies have been developed over the past years, including intra- and intermolecular cyclization reactions, each with their specific advantages and disadvantages.11 Representative intramolecular reactions include ring expansion of suitably substituted cyclopropenes,12 Friedel−Crafts cyclization of allyl13 and propargyl alcohol derivatives,14 aromatic 1,3 dienes,15 and αβ unsaturated ketones.16 Other methods include oxidative cyclizations,17 palladium catalyzed intramolecular Heck type couplings,18 ring-closing metathesis,19 aromatic C−H bond functionaliza-
A series of intermolecular approaches have also been developed for indene synthesis, including [3 + 2] annulation of aryl alkynes with benzyl derivatives,\textsuperscript{24} carbynyls,\textsuperscript{25} alkenes and dienophiles,\textsuperscript{26} palladium-catalyzed carboacyclization of aryl halide/boronic acids and alkynes,\textsuperscript{27} Fe-catalyzed cyclization of benzyl and substituted alkynes and alkenes,\textsuperscript{28} noble metal catalyzed aromatic C–H bond activation cyclization,\textsuperscript{29} and copper catalyzed radical cyclizations.\textsuperscript{30} However, several of these existing methods suffer from functional group intolerance, the necessity of expensive (noble) transition metal catalysts, harsh reaction conditions and/or are limited to the synthesis of specific indenes with a particular substitution pattern. Hence, in need of a broader pallet of synthetic methodologies the development of new, short, efficient, and broadly applicable catalytic routes to expand the currently available methods for indene synthesis from readily available starting materials is certainly in demand, especially those employing benign, readily available and inexpensive base metal catalysts.

As stable metalloradicals with well-defined open-shell doublet d\textsuperscript{−}−electronic configuration, low-spin planar cobalt(II) complexes have recently emerged as a new class of catalysts capable of “carbene-transfer” reactions proceeding via radical mechanisms involving discrete Co\textsuperscript{II}−carbene radical intermediates (Figure 2). Metalloradical activation of carbene precursors (such as diazo compounds or N-tosylhydrazones) produces carbenoids with radical-character at the respective “carbene” carbon, enabling catalytic radical-type organometallic transformations.\textsuperscript{31−36} These carbene-radical intermediates are best described as one-electron reduced Fischer-type carbenes, and as a result they have characteristics of both electrophilic Fischer-type carbenes) upon reacting planar, low spin cobalt(II) complexes with carbene precursors.

![Figure 2. Formation of Co\textsuperscript{III}−carbene radicals (one-electron reduced Fischer-type carbenes) upon reacting planar, low spin cobalt(II) complexes with carbene precursors.](image)

RESULTS AND DISCUSSION

Our initial attempt to synthesize a substituted 1H-indene involved reaction of o-cinnamyl N-tosyl hydrazone (1a) in the presence of the commercially available [Co\textsuperscript{III}(TPP)] catalysts (at a temperature of 60 °C, unless indicated otherwise). Different bases such as LiO\textsubscript{Bu}, KO\textsubscript{Bu}, NaO\textsubscript{Bu}, K\textsubscript{2}CO\textsubscript{3}, NaOMe (Table 1, entries 1−5) can be used to activate the N-tosyl hydrazone in chlorobenzene, but with LiO\textsubscript{Bu} the highest yield of the desired 1H-indene product 2a was obtained (51%; entry 1).

Upon increasing the amount of base (LiO\textsubscript{Bu}) from 1.2 to 3 equiv the yield dropped substantially (Table 1, entries 1, 6−7).

![Table 1. Standardization of Reaction Conditions](image)

Yields were determined by integration of the 1H NMR signals in the presence of acenaphthene as internal standard. Reaction carried out at room temperature.
This is probably caused by decomposition or poisoning of the catalyst in the presence of excess base. To improve the yield of the reaction different cobalt(II) sources were investigated. The fluorinated porphyrin and salen based cobalt catalysts (Table 1, entry 8, 10) did not produce the desired product, but the cheap and easy to prepare [CoII(MeTAA)] catalyst (Figure 2) produced 1H-indene 2a in excellent yield (83%) using toluene as the solvent (Table 1, entry 9).

[CoII(MeTAA)] is the cobalt(II) complex of the tetramethyltetraaza[14]annulene (MeTAA) ligand (Figure 3).

Figure 3. Structures of the cobalt(II) catalysts used in this study.

The complex was first prepared in 1976,38 involving two simple steps to obtain the complex in near quantitative yield. This is in sharp contrast to the synthesis of porphyrin complexes, which is in general work-intensive, low yielding, time-consuming and produces large amounts of unwanted side products, thus demanding elaborate (column chromatographic) purification steps. The MeTAA ligand has similar bonding properties as a porphyrin, which reflects in its ability to bind a variety of transition metals.39,40 However, there are also some differences which likely explain its increased reactivity as compared to [Co(TPP)]. While porphyrins have an aromatic (4n+2) delocalized π-cloud, MeTAA is Hückel antiaromatic (4n), which increases the flexibility of the ligand. Another difference between these two macrocyclic structures is their ring size (14- vs 16-membered ring). The increased flexibility and smaller ring-size of MeTAA as compared to a porphyrin leads to deviation from planarity, and as such [CoII(MeTAA)] adopts a saddle shaped configuration.

Other catalysts such as [CuI] or [Rh2(OAc)4] (Table 1, entries 11−12) proved less or not effective. Quite surprisingly the carbene transfer catalyst [Rh2(OAc)4], which is well-known to be operative in a variety of carbene C−H bond insertion reactions,35 produced no indene at all. In general, carbene insertion into vinyllic C(sp2)−H bonds is extremely rare if not entirely unprecedented, likely because cyclopropanation is favored for other (nonmetalloradical) carbene transfer catalysts. Notably, CuI did catalyze the reaction to some extend but produced only 27% of the desired indene, with mainly the carbene−carbene dimerized product being formed in the undesired side reaction.

Extended solvent screening revealed that the reaction works best in nonpolar solvents such as benzene, toluene, or hexane (entries 9, 14, 18). Most polar solvents such as CH2Cl2 or CH3CN (entries 16−17) led to comparatively low yields, but THF works well as a solvent (entry 15). The reaction does not produce 2a without a catalyst (entry 19), and the yield of the reaction drops drastically when performing the reaction at room temperature (entry 20). Conversion of the N-tosyl hydrazone into the corresponding diazo compound accounts for at least part of the required activation energy.37

To explore the scope of the metalloradical catalyzed indene synthesis, several different functional groups were introduced at the vinylic double bond (Table 2). Several α,β-unsaturated esters are tolerated (i.e., the Et-, nBu-, iBu-, and Ph-esters 1a−e), producing indenes 2a−e in good to excellent yields (78−86%, entries 1−5) using the standardized reaction conditions shown in Table 2. Surprisingly, α,β-unsaturated amide 1f produced indene 2f in even higher yield (98%; entry 6), and also styrene derivative 1h furnished the corresponding indene product 2h in good yield (85%; entry 8). The α,β-unsaturated nitrile substrate 1g works less well, producing indene 2g in moderate yield (52%; entry 7).

The substrate scope was further explored and broadened by investigating the effect of varying the substituents on the aromatic ring (Table 3). Substitution at the 5- or 6-position of the aromatic ring does not affect the yield of the products 2i (Table 3, entries 1−2). Electron withdrawing substituents such as −F, −Cl, −CF3, and −NO2 are all effective, affording the corresponding indenes 2i−l in good to excellent yields (Table 3, entries 1−5). Reactions proceeded even better with neutral electron-donating groups on the aromatic ring such as naphthyl (1n) and methyl (1o) groups producing the corresponding indenes 2m,n in excellent yields (Table 3, entries 6−7). Substrates 1p,q bearing 5-methoxy and 4,5-dimethoxy substituents produced indenes 2o,p in a somewhat lower yield (~70%).

For most of the asymmetrically substituted substrates shown in Table 3 (except entry 10) both possible regio-isomers of products 2i−p are formed in a nearly 1:1 ratio. This points to allylic/benzylic double bond isomerization under the applied reaction conditions, as can be expected for 1H-indenes having rather acidic allylic/benzylic protons. Substitution at the allylic/benzylic position has also been investigated. Interestingly

<table>
<thead>
<tr>
<th>Entry</th>
<th>R-</th>
<th>Products</th>
<th>Yield%</th>
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<tr>
<td>1</td>
<td>-COOMe (1a)</td>
<td>COOMe (2a)</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>-COOEt (1b)</td>
<td>COOEt (2b)</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>-COO′Bu (1c)</td>
<td>COO′Bu (2c)</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>-COO′Bu (1d)</td>
<td>COO′Bu (2d)</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
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<td>COOPh (2e)</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>-CONMe2 (1f)</td>
<td>CONMe2 (2f)</td>
<td>98</td>
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<tr>
<td>7</td>
<td>-CN (1g)</td>
<td>CN (2g)</td>
<td>52</td>
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<tr>
<td>8</td>
<td>-Ph (1h)</td>
<td>Ph (2h)</td>
<td>85</td>
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</table>

*Reaction conditions: N-tosylhydrazone (1a−h) (0.2 mmol, 1.0 equiv), LiO′Bu (0.24 mmol, 1.2 equiv), [Co(MeTAA)] (5 mol %), benzene (3 mL), 60 °C, overnight. Isolated yields after column chromatography.
reacting N-tosylhydrazone 1s results in regioselective formation of indene product 3 in high yield (Table 3, entry 10) with the double bond at the thermodynamically favored most substituted position.

Full statistical (thermodynamically controlled) scrambling of the allylic and vinylic protons under the applied (alkaline) reaction conditions was confirmed by the deuterium-labeling experiments shown in Scheme 1. Starting either with a deuterium label at the azomethine position (1a-D) or at the vinylic position (1b-D) of the carbenoid precursor leads in both cases to a complete statistical distribution of the deuterium atoms over the allylic/benzylic and vinylic positions, as indicated by a 2:1 ratio of the \(-\text{CDH}\) and –CD signals in the D-NMR spectra of deuterium-labeled indene products 2a-D/2a′-D and 2b-D/2b′-D (Scheme 1).

To shed more light on the catalytic reaction mechanism, we explored the mechanism computationally. Additionally we performed a set of trapping and control experiments, combined with EPR spectroscopic investigations.

At first sight the reaction may seem to proceed via a direct carbene insertion into the vinylic C(sp\(^2\))–H bond. However, such reactions are unprecedented to the best of our knowledge, and \([\text{Rh}_2(\text{OAc})_4]\) (which is well-known for its reactivity in aromatic and aliphatic C–H bond functionalization by direct carbene insertion) is not active in 1H-indene formation (vide supra). In addition, attempts to find a transition state for this process for the \([\text{Co(MeTAA)}]\) catalyst with DFT were unsuccessful, and the electronic structure of a Co\(^{\text{III}}\)-carbene radical in general (Figure 2) seems to be incompatible with any direct, concerted C–H insertion mechanism of the carbenoid. Hydrogen atom transfer from the vinylic C–H bond to the carbene radical followed by a radical rebound step could in principle be an alternative, but all attempts to optimize such a vinyl radical intermediate (D′ in Scheme 2) converged back to carbene radical C, thus indicating that the route via D′ is not a viable pathway. As such, a metalloradical pathway involving

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**Table 3. Substrates Scope Bearing Various Functional Group on Aromatic Ring**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>Products</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>(1i)</td>
<td>(2i)</td>
<td>87c</td>
</tr>
<tr>
<td>2</td>
<td>(1j)</td>
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<td>85c</td>
</tr>
<tr>
<td>3</td>
<td>(1k)</td>
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<td>(1l)</td>
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<td>5</td>
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<tr>
<td>10</td>
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<td>(3)</td>
<td>95c</td>
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</tbody>
</table>

*Reaction conditions: N-tosylhydrazone (1i–s) (0.2 mmol, 1.0 equiv), LiO\(\text{Bu}\) (0.24 mmol, 1.2 equiv), CoMeTAA (5 mol %), benzene (3 mL), 60 °C, overnight. *Isolated yields after column chromatography. *Nearly 1:1 ratio of both isomers formed.
attack of the carbene radical at the vinylic double bond to form
the cyclized $\gamma$-radical intermediate D seems to be the most
plausible mechanism. This mechanism was fully explored for
both the [Co(MeTAA)] and [Co(TPP)] catalysts with DFT-
D3 at the BP86, def2-TZVP level, using Grimme’s version
dispersion corrections (disp3). The selected computational
method is in agreement with our previous studies involving
Co(III)-carbene radicals as intermediates in catalytic cycliza-
tions, and is known to provide accurate Co−C BDEs.42

The computed mechanism for the [Co(MeTAA)] catalyst is
presented in Scheme 2. The corresponding mechanism for the
[Co(TPP)] catalyst and the associated energy diagrams of the
reactions with both catalysts are shown in the Supporting
Information (Figure S1). All steps have accessible barriers, and
each step is exergonic.

The first steps of the DFT computed reaction mechanism
involve trapping and activation of the in situ generated diazo
compound by the [Co(MeTAA)] catalyst (Scheme 2). Formation of the Co$^{II}$-catalyst-diazo adduct B is exergonic
($\Delta G^o = -11.6$ kcal mol$^{-1}$), as is N$_2$-elimination from B to
produce the Co$^{III}$-carbene radical species C ($\Delta G^o = -14.7$ kcal
mol$^{-1}$). The transition state barrier for formation of C from B is
low (TS1; $\Delta G^\ddagger = +7.4$ kcal mol$^{-1}$). These steps are similar to
those reported previously in the mechanisms for 2$H$-chromene
formation$^{36}$ and cyclopropanation$^{31}$ using Co$^{II}$-porphyrin
catalysts.

The next step involves addition of the carbene radical to the
vinylic double bond producing the cyclized $\gamma$-radical intermediate D ($\Delta G^o = -17.7$ kcal mol$^{-1}$) via transition state
TS2 (barrier: $\Delta G^\ddagger = +18.9$ kcal mol$^{-1}$). This appears to be the
rate limiting step of the catalytic cycle. Indene formation from
D requires a low barrier 1,2-hydrogen atom transfer (TS3; $\Delta G^\ddagger = +13.8$ kcal mol$^{-1}$), relocating the radical from the $\gamma$- to the $\beta$-
position. The thus formed cobalt-bound $\beta$-radical species is so
unstable that it spontaneously dissociates in a barrierless
manner to form indene product E. The overall process is
strongly exergonic ($\Delta G^o = -58.4$ kcal mol$^{-1}$).

Scheme 2. Proposed Mechanism of [Co(MeTAA)] Catalyzed 1$H$-Indene Synthesis$^{44}$
An alternative pathway for indene formation from D is possible, involving dissociation of the de aromatized (methide-like 2H-indene) E′ from D, followed by 1,2 hydride shift (TS4) to produce the 1H-indene product E (Scheme 2). Dissociation of E′ from D involving homolytic splitting of the Co−C bond to produce starting complex A is endergonic by about +13 kcal mol\(^{-1}\) according to DFT (the reverse reaction is barrierless), but coordination of substrate 1a′ to A producing B makes the overall process virtually thermoneutral. Subsequent conversion of E to E′ has a low barrier transition state (TS5; \(\Delta G^\ddagger = +10.4\) kcal mol\(^{-1}\)). The computed pathways for indene formation from D via E′ (\(\Delta G^\ddagger = +12.7\) kcal mol\(^{-1}\); determined by dissociation of E′ to form A) and the direct pathway over TS3 (\(\Delta G^\ddagger = +13.8\) kcal mol\(^{-1}\)) have very similar overall barriers, and thus seem to be competing trails producing the same product.

Spin density plots of the key intermediates C and D are presented in Figure 4. Most spin density is ligand centered for both intermediates. For intermediate C the highest spin population is found on the carbenoid carbon atom, in agreement with a Co\(^{III}\)-carbene radical electronic structure as presented in Figure 2. In intermediate D the largest spin population is found at the \(\gamma\)-position, with some delocalization over the adjacent phenyl moiety. Both structures have less than 10% spin population at cobalt, thus showing that radical-type elementary steps involving coordinated substrate radicals play a key role in the catalytic mechanism.

To obtain additional information about the mechanistic pathway we attempted to trap intermediates with radical scavengers.\(^{43}\) In agreement with the above DFT calculations indicating that Co\(^{III}\)-carbene radical intermediate C is the catalytic resting state, these trapping experiments produced in all cases products stemming from species C (Scheme 3).

Reacting substrate 1a with [Co(MeTAA)] in the presence of three equivalents of TEMPO under identical reaction conditions as used in catalytic indene synthesis led to formation of product 5 (Scheme 3). Compound 5 was isolated, purified by column chromatography and characterized by \(^1\)H, \(^{13}\)C and GCMS spectroscopy (see Supporting Information). The compound has a TEMPO moiety attached to the carbon stemming from the “carbene”, which is (over)oxidized to a carbonyl group. The use of dibenzoylperoxide as a radical scavenger also led to trapping of carbene radical intermediate C, in this case leading to formation of product 7 (Scheme 3). No ring-closed intermediates could be trapped, consistent with TS2 being the rate limiting step in the DFT calculated mechanism with all follow-up steps after formation of D being fast (Scheme 1). Cold spray electron spray ionization high resolution mass spectrometry (ESI-HRMS) experiments of the catalytic reaction mixture in absence of radical scavengers are in agreement with the presence of carbenoid species C (Scheme 2). The detected mass \(m/z = 576.1906\) (calc. \(m/z = 576.1936\)) corresponds to \([\text{C}+\text{H}]^+\) (\(\text{C}_8\text{H}_{13}\text{CoN}_3\text{O}_2\)), and can be attributed to protonated species C.

Spin trapping experiments using phenyl \(N\)-tert-butyl nitronate (PBN) as the spin trap support the proposed radical-type mechanism. Heating a mixture of 1a, [Co(MeTAA)], LiO\(\text{Bu}\) in the presence of PBN led to formation of PBN-trapped carbon-centered radicals as detected with EPR spectroscopy (Figure 5).

The resulting EPR signal (\(g = 2.0063\), \(A_N = 14.4\) G, \(A_H = 2.8\) G) is strong and similar to other reported PBN-trapped carbon centered radicals.\(^{44}\) Heating the reaction mixture in absence of cobalt (i.e., noncatalytic conditions, in which case no indene formation occurs) also some PBN-trapped radicals were detectable, but different ones with weaker intensity (see Supporting Information).

**CONCLUSIONS**

Metalloradical activation of a series of \(o\)-cinnamyl-N-tosyl hydrazones produces a variety of functionalized 1H-indenes in high yields and with a broad functional group tolerance. The reaction uses readily available starting materials and is operationally simple, thus representing a practical method for the construction of substituted 1H-indene derivatives. The cheap and easy to prepare low spin cobalt(II) complex [Co(MeTAA)] proved to be the most active catalyst among those investigated, showcasing for the first time catalytic activity of this complex in general. DFT studies reveal a stepwise process involving activation of the diazo compound leading to formation of a carbene radical intermediate, which is then converted to an indene derivative through a series of radical-type elementary steps.

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**Scheme 3. Radical Scavenging Experiments Used to Trap the Co\(^{III}\)-Carbene Radical Intermediate**

![Scheme 3](image-url)
formation of a CoIII-carbene radical, followed by a rate limiting radical ring-closure step to produce an indanyl-radical intermediate. Subsequent 1,2-hydrogen atom transfer leads to elimination of the 1H indene product and regenerates the CoII catalyst. The computed mechanism was confirmed by a series of supporting radical-scavenging experiments. Deuterium labeling experiments further reveal statistical scrambling of the allylic/benzylic and vinylic protons under the applied reaction conditions. The metallo-radical catalyzed indene synthesis in this paper represents a rare example of a net, formal (intramolecular) carbene insertion reaction into a vinylic C(sp2)−H bond, made possible by taking advantage of the distinctive and controlled reactivity of the key CoIII-carbene radical intermediates involved. Further studies aimed at exploring the controlled organometallic radical-type reactivity of transition metal carbene radicals in ring-closing reactions and C−H bond functionalization are underway.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05434.

Compound characterization data (NMR, HRMS, etc.), absolute energies (atomic units), coordinates of the DFT-optimized structures (PDF)

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**Author Contributions**

† BGD and AC contributed equally.

**Notes**

The authors declare no competing financial interest.

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