

# Synthesis of 6*H*-Benzo[*c*]chromene Scaffolds from *O*-Benzylated Phenols through a C–H Sulfenylation/Radical Cyclization Sequence

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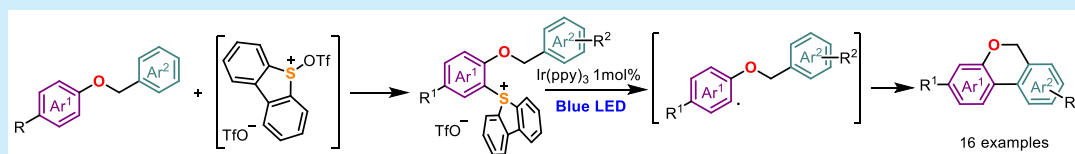
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**ABSTRACT:** *S*-Aryl dibenzothiophenium salts, obtained through a highly regioselective C–H sulfenylation of *o*-benzyl-protected phenols, are used as precursors of 6*H*-benzo[*c*]chromenes. The reaction starts with a photocatalytically triggered single-electron transfer to the sulfonium salt, which promotes the formation of an aryl radical via selective mesolitic cleavage of the S–Ar<sub>exo</sub> bond. Mechanistic studies reveal that this initial radical species cyclizes following a kinetically favored 5-*exo*-trig pathway. Subsequent ring expansion, favored by rearomatization, delivers the desired tricyclic systems.

The ability of sulfonium salts to generate organic radicals after accepting one electron via mesolitic S–C bond cleavage was reported by Kellogg as early as 1978. Although the specific transformation chosen in his study, namely, the desulfuration of phenacyl sulfonium salts **1** to acetophenones, has limited synthetic applications, the seminal work already contained all of the ingredients that later contributed to the flourishing of photoredox catalysis into a versatile synthetic tool (Scheme 1a).<sup>1</sup> After that original finding, the further employment of sulfonium salts in the photocatalysis arena remained dormant for decades until Fensterbank, Goddard, and Ollivier, making use of the conditions developed by Kellogg, reported the formation of aryl radicals from triaryl sulfonium salts **2**.<sup>2</sup> Interestingly, the thus-prepared radicals were found to participate in carbon–carbon bond-forming reactions, including allylation and addition to olefins; however, the scope and practical utility of their protocol was severely limited to structurally simple and easily available aryl groups. Note that whereas the three aryl substituents at the central sulfur of the sulfonium salt need to be identical to avoid chemoselectivity issues, only one of them can finally be transferred (Scheme 1b).

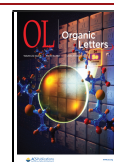
That contribution attracted the attention of many researchers toward the chemistry of sulfonium salts, and a number of investigations followed, in particular, those focused on the generation of benzyl radicals.<sup>3</sup> However, it has not been until very recently that the full synthetic potential of sulfonium salts could be exploited by the identification of suitable platforms, such as the dibenzothiophene and thianthrene skeletons, which chemoselectively promote the cleavage of the S–Ar<sub>(exo)</sub> bond after a single-electron transfer process.<sup>4</sup> This has significantly increased the range of applications of sulfonium salts.<sup>5</sup> Among the recently developed trans-

formations, the metal-free C–H cross-coupling between unfunctionalized (hetero)arenes arguably stands out for its synthetic potential and simplicity (Scheme 1c).<sup>4a</sup> It also worth noting that all of these newly developed transformations enormously benefit from the recently developed routes for the synthesis of sulfonium salts from unfunctionalized arenes via highly regioselective C–H sulfenylation.<sup>6,7</sup>

Being aware of the practical utility of the two-step C–H sulfenylation/Ar-radical generation strategy just mentioned, we envisaged the possibility of transforming that methodology into an efficient cyclization tool when applied to appropriately designed polyaromatic substrates. Crucial for the success of this concept is the initial sulfenylation step, which must be highly regioselective. In fact, the substrate needs to be engineered in a way that the sulfenylation occurs only at the position that geometrically allows the subsequent radical cyclization, and this must occur in the presence of at least two different aromatic rings. Not making things easier, the conditions need to be settled in a way that the transient radical intermediate cyclizes in the predicted manner and does not evolve via any other plausible competing reaction pathway.<sup>8</sup> Considering all of these requirements, *p*-substituted aryl benzyl ethers **4** were selected as appropriate model substrates, which should reliably undergo sulfenylation at the *o*-position of the phenol moiety to deliver sulfonium salts **5**. The subsequent

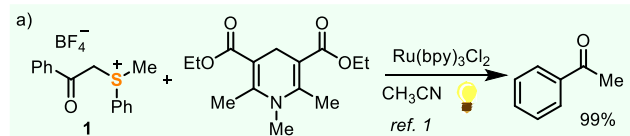
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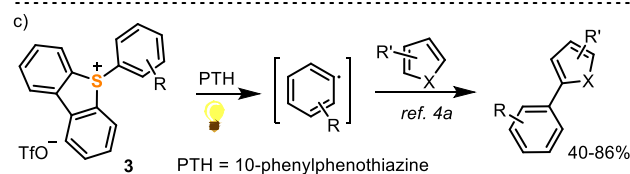
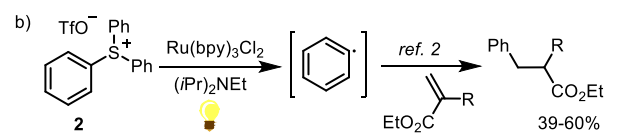


### Scheme 1. Selected Precedents in Photocatalytic Radical Generation Using Sulfonium Salts

#### Seminal work



#### C-C bond formation



#### This work: Selective sulfenylation + Intramolecular C-H arylation

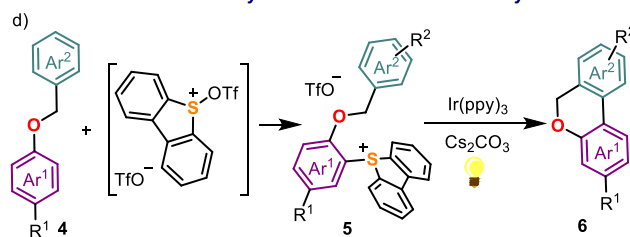
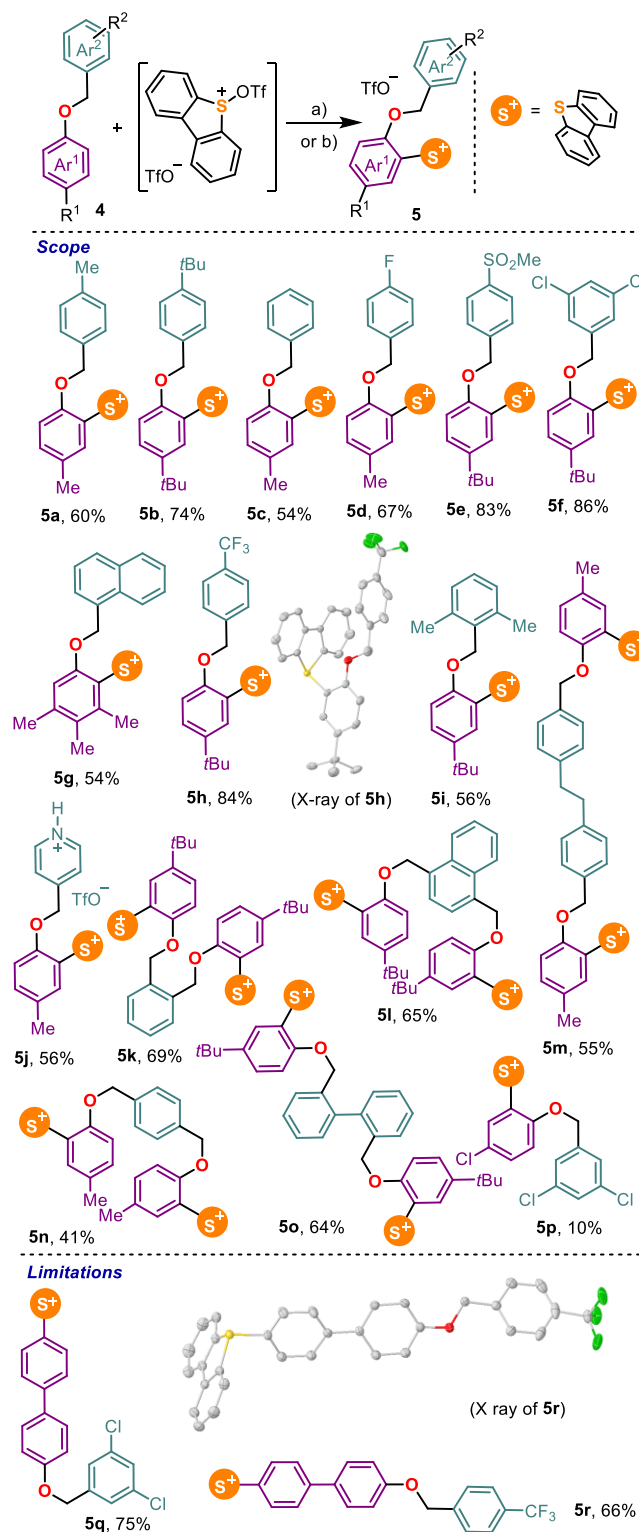


photo-redox-promoted radical generation is expected to initiate a Pschorr-type cyclization to afford the desired 6*H*-benzo[*c*]chromenes (Scheme 1d).<sup>9,10</sup> Herein we report the practical realization of that initial hypothesis as well as a series of control experiments focused on determining the actual reaction path operative under the applied conditions.

To our delight, the initial sulfenylation step proceeds as programmed, and a range of *O*-benzylated phenols are selectively functionalized at the *o*-position of the oxygenated substituent **5a–j,p** (Scheme 2). Note that alkyl groups (Me- or *t*Bu-) are needed to block the otherwise more sterically accessible *p*-position of the most electron-rich ring. Halogens and phenyl and methoxy groups are not adequate for this task; the former dramatically reduces the yield of the reaction (**5p**), whereas the latter suffer sulfenylation themselves; see compounds **5p–r**. Complex reaction mixtures are obtained when additional methoxy groups are installed in the substrates. Yields of **5a–j** are moderate to good, and all compounds survive column chromatography purification on silica gel despite their saline nature. Bis-sulfonium products **5k–o** are also obtained in acceptable yields provided that a slight excess of the sulfenylation reagent is employed. The connectivity of the newly prepared products has been additionally confirmed by X-ray analyses of compounds **5e,f,h,i,r**. (See Scheme 1 for **5h** and **5r** and the Supporting Information for the others.) Short contacts between the sulfur atom and one oxygen from the triflate counteranion are detected along the complete series, revealing the remarkable electrophilic character of sulfur in these compounds.<sup>6b</sup>

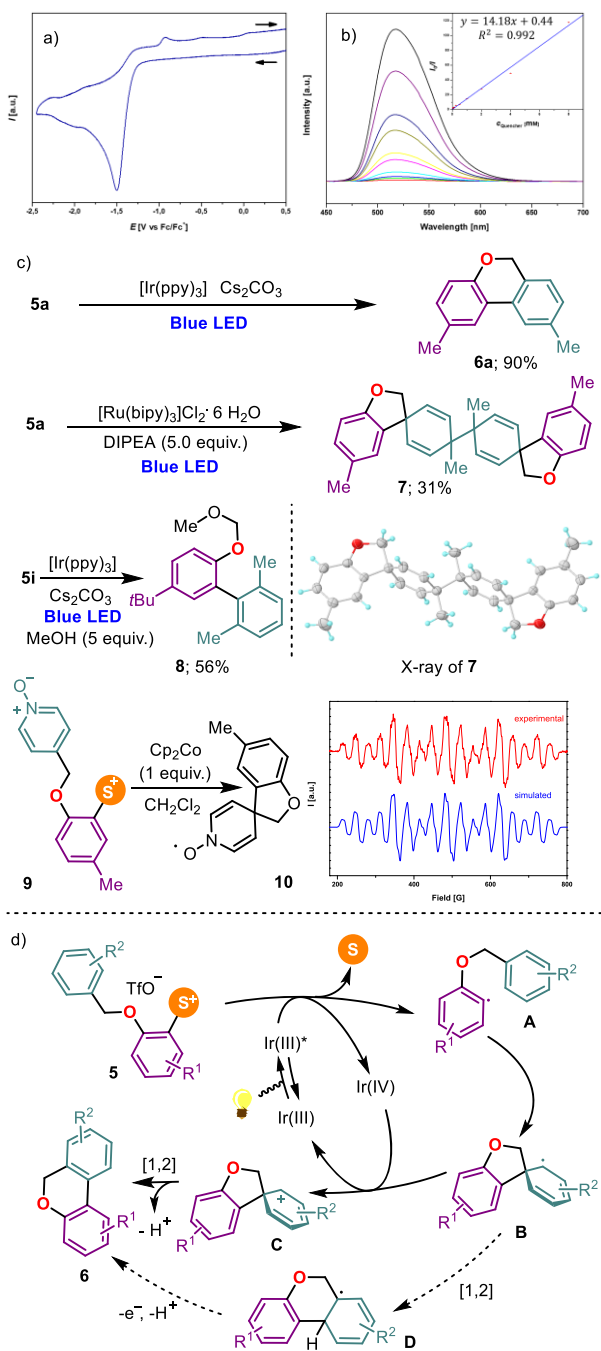
In this stage, we continued the characterization of the obtained salts by determining the reduction potential of model substrate **5a** through cyclic voltammetry (CV). This experi-

### Scheme 2. Scope of the Sulfenylation Step<sup>4a</sup>



<sup>4a</sup>Reaction conditions: (a) arene (1.1 equiv), pyridine (1.1 equiv) in CH<sub>2</sub>Cl<sub>2</sub>, -60° → r.t., 16 h; b) arene (0.5 equiv), pyridine (1.05 equiv) in CH<sub>2</sub>Cl<sub>2</sub>, -60° → r.t., 16 h. For the X-ray structures of **5h** and **5r**, ellipsoids are represented at 50% probability, and triflate anions and hydrogen atoms are omitted for clarity.

ment showed an irreversible reduction with  $E_{\text{red}} = -1.50$  V (vs Fc<sup>+/0</sup> in CH<sub>3</sub>CN) (Scheme 3a).<sup>4a</sup> This value is considerably less negative than that determined for the excited state of

Scheme 3. Mechanistic Studies<sup>a</sup>

<sup>a</sup>For the X-ray structure of **7**, ellipsoids are represented at 50% probability.

$\text{Ir}(\text{ppy})_3$  ( $E_{\text{red}}^* = -2.13 \text{ V vs Fc}^{+/0}$  in  $\text{CH}_3\text{CN}$ ) or that of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  after photoexcitation and reductive quenching ( $E_{\text{red}} = -1.73 \text{ V vs Fc}^{+/0}$ ), indicating the feasibility of the necessary single-electron transfer event from the catalyst to the substrate in both cases.<sup>11</sup> In line with these findings, Stern–Volmer experiments confirm that **5a** effectively quenches the excited state of  $\text{Ir}(\text{ppy})_3$  (Scheme 3b). Actually, both catalytic systems promote the formation of transient aryl radicals via C–S bond cleavage; however, while  $\text{Ir}(\text{ppy})_3$  efficiently transforms the model substrate **5a** into the desired 6*H*-benzo[*c*]chromene **6a**, the combination of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  and

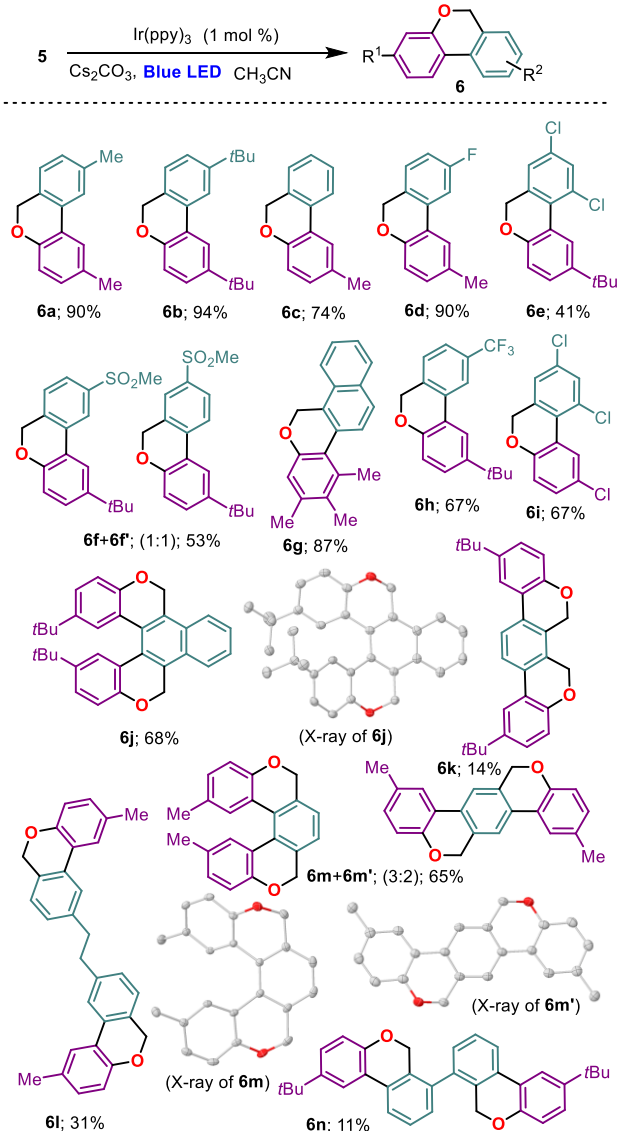
DIPEA (5.0 equiv) mainly delivers the dimeric structure **7** (Scheme 3c).

Control experiments and cumulative evidence from the literature indicate that the operating mechanism is, with high probability, the one shown in Scheme 3d.<sup>4a,8,10</sup> Preliminary experiments indicate that the reaction does not proceed in the dark, and the quantum yield of the formation of **6a** is 0.47, suggesting that a radical chain process cannot predominate.<sup>12</sup> Hence, we do believe that upon the initial generation of radical **A**, a kinetically favored 5-exo-trig ipso-attack of the aryl radical to the pending arene results in the formation of spiro cyclohexadienyl radical **B**. The installation of a pyridine-*N*-oxide substituent as a radical trapping agent in the substrate allows the detection of species of this structure.<sup>13</sup> Thus, the reaction of sulfonium salt **9** with 1 equiv of  $\text{Cp}_2\text{Co}$  ( $E_{\text{red}} = -1.33 \text{ V vs Fc}^{+/0}$ ) affords radical **10**, which we have characterized by standard electron paramagnetic resonance (EPR) techniques. Its spectrum shows resolved hyperfine splitting as result of hyperfine coupling to the N atom ( $a_{\text{N}} = 8.39 \text{ G}$ ) and two pairs of equivalent H atoms ( $a_{\text{H}} = 5.83$  and  $1.99 \text{ G}$ , respectively). This pattern fits with that expected for the  $C_s$  symmetric structure of **10**.

Another hint indicating the formation of **B** comes from the isolation of substantial amounts of its dimer **7** when **B** is formed under the reducing environment generated by the  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{DIPEA}$  catalytic system. Under the applied conditions, this mixture is not capable of effectively promoting the further reduction of **B** ( $E_{1/2} = -1.74 \text{ V vs Fe}^{+/0}$ ) into the corresponding cyclohexadienyl anion<sup>8a</sup> or its oxidation to **C**. For that reason, **B** accumulates and finally dimerizes. The isolation of **7**, and not a dimer of **D**, also indicates that the [1,2]-aryl migration must be a slow process under our working conditions, in the case that it actually takes place. Moreover, the evolution of **B** into **D** is reported to be nonselective, delivering regioisomeric product mixtures.<sup>14</sup> We have observed the formation of regioisomeric mixtures only in the case of **6f** and **6f'** (Scheme 4). Hence, we proposed that this reaction preferentially proceeds via the oxidation of **B** into carbocation **C**, followed by [1,2]-aryl rearrangement and deprotonation to deliver **6**.<sup>4a</sup> On the contrary, the sulfone substituent in the precursor of **6f** and **6f'** is expected to hinder the oxidation of this species from **B** to **C**. In that case, the ring expansion step probably takes place at the radical intermediate, resulting in a low-selectivity process.

Finally, we have also submitted to standard reaction conditions substrate **5i**, which has been conveniently designed with two methyl substituents at the *o*-positions of the tether. Because 1,2-migration is hindered here, a scission of the  $\text{CH}_2\text{-C}_{\text{spiro}}$  bond takes place, and the thus-generated intermediate is trapped with MeOH, delivering the MOM-protected biaryl **8** (Scheme 3c).

This light-driven reaction effectively engages a range of substrates **5a–o** in the desired cyclization toward 6*H*-benzo[*c*]chromenes in good to excellent yields (Scheme 4). Fluoro, chloro, sulfone, and trifluoromethyl substituents are tolerated, which allows the further functionalization of the products obtained, for example, by traditional cross-coupling chemistry. The scalability of the protocol has been demonstrated by the preparation of **6a** on a scale ten times higher than the initial scale (350 mg) with no loss of yield; moreover, dibenzothiophene (96%) is recovered from that experiment and can be recycled.

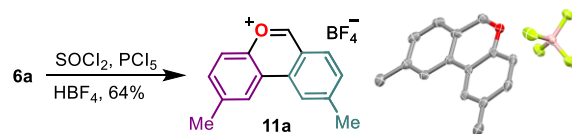
Scheme 4. Scope of the Photocatalyzed Cyclization<sup>a</sup>

<sup>a</sup>For the X-ray structures of 6j, 6m, and 6m', ellipsoids are represented at 50% probability. Triflate anions and hydrogen atoms are omitted for clarity.

Double cyclizations also proceed satisfactorily; however, the second [1,2]-rearrangement from intermediate C to 6 is not regioselective when the adjacent positions to the spiranic carbon are not chemically equivalent (6m, 6m'). In these cases, mixtures of the helicoidal and linearly cyclized regioisomers are observed. The connectivity of both types of products is confirmed by X-ray diffraction analyses (Scheme 4). The Supporting Information contains the X-ray structure of 6b. The free energy of activation ( $\Delta G^\ddagger$ ) for the inversion of the helicoidal structure 6j is estimated by temperature-dependent nuclear magnetic resonance (NMR) to be 81.2 kJ/mol. From this number, it can be deduced that the half life at 20 °C of the enantiomers is approximately half a minute, making their separation impossible at this temperature.

Finally, to further explore the synthetic utility of the method reported, 6a is further transformed into the corresponding pyrylium salt 11a by the reaction with  $\text{SOCl}_2/\text{PCl}_5$  (Scheme 5).<sup>15</sup> These salts are well known precursors of condensed

polyaromatic structures, phosphorines, and pyridinium and thionium salts.<sup>16</sup>

Scheme 5. Synthesis of Pyrylium Salts From 6a<sup>a</sup>

<sup>a</sup>For the X-ray structure of 11a ellipsoids are represented at 50% probability. Triflate anions and hydrogen atoms are omitted for clarity.

In summary, a mild and efficient protocol for the rapid synthesis of 6H-benzo[c]chromenes is described, which operates via the selective C–H sulfenylation of electron-rich aromatic moieties followed by photocatalyzed radical cyclization. The utility of the method, which also allows multicyclizations, is exemplified by the synthesis of 6H-benzo[c]chromenes of different substitution patterns and their one-step transformation into synthetically versatile pyrylium salts.

## ■ ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c00087>.

General experimental procedures, characterization data including  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra of new compounds, and dynamic NMR studies (PDF)

## Accession Codes

CCDC 2051252–2051263 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto: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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