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# Transition-Metal-Free Allylic Borylation of 1,3-Dienes

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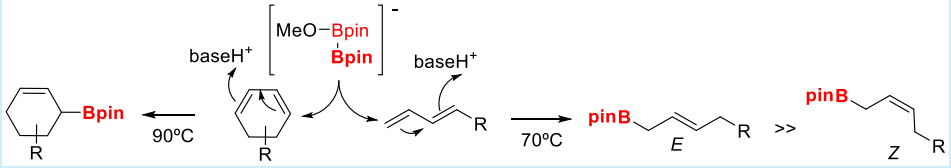
Supporting Information




**ABSTRACT:** This work explains the reactivity of diboron reagents with 1,3-dienes in a transition-metal-free context. The sole addition of $Na_2CO_3$ (30 mol %) to bis(pinacolato)diboron in MeOH allows the 1,4-hydroboration of cyclic and noncyclic 1,3-dienes. The electronic influence on the substrate guarantees the conjugated 1,4-hydroboration versus 1,2-diboration. DFT calculations show that the distribution of charge in the allylic anion intermediate governs the selectivity toward 1,4-hydroboration, while the favored *trans* configuration in diene reagents determines the preference for the *E* allyl boronate products.

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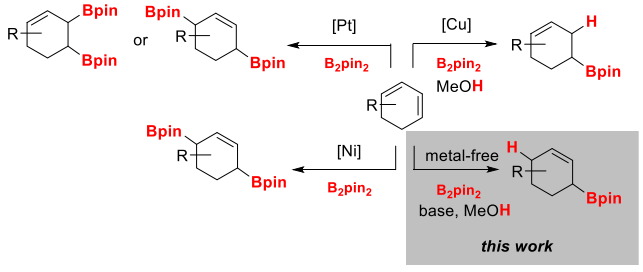
The borylation of 1,3-dienes represents a powerful synthetic tool to obtain diborated or monoborated allylic systems, depending on the transition-metal catalyst employed. From Miyaura and co-worker's breakthrough experiments on $Pt(PPh_3)_4$-catalyzed 1,4-diboration of 1,3-dienes to synthesize bis(allyl)boronates,[1] the field has progressed by discovering different catalytic systems based on Pt, Ni, and Cu. The most explored strategy uses Pt complexes to catalyze both 1,2- and 1,4-diboration of 1,3-dienes, even in an asymmetric fashion.[2,3] Nickel complexes are also explored as catalytic systems, and unlike Pt complexes, the Ni catalytic systems can catalyze the 1,4-selective diboration of even sterically hindered 1,3-dienes.[4] Contrary to Pt or Ni complexes, the Cu complexes catalyze the monoboration of 1,3-dienes with $B_2pin_2$ primarily forming the homoallyl boronate products (Scheme 1).[5,6]

Here, in this work, we present the results of the borylation of 1,3-dienes in a transition-metal-free context, with the sole addition of MeOH and base to generate the corresponding methoxide and form the adduct [MeO-Bpin-Bpin]$^-$[Hbase]$^+$ (Scheme 1, bottom right). Transition-metal-free borylation reactions have emerged within this decade as a convenient synthetic methodology toward selective C–B bond formation.[7] Our group has previously explored the allylic borylation of tertiary allylic alcohols[8] as well as the allylic borylation of vinyl epoxides and vinyl aziridines[9] by the addition of the acid–base Lewis adduct [MeO-Bpin-Bpin]$^-$[Hbase]$^+$ through $S_N2'$-type mechanisms. To the best of our knowledge, the borylation of 1,3-dienes without metal catalysts was only precedented through the uncatalyzed diboration of 1,3-butadiene using the highly reactive $B_2Cl_4$ or $B_2F_4$ to produce 1,4-bis-(dihalogenoboryl)-2-butene compounds.[10,11]

**Scheme 1. Previous Transition-Metal-Catalyzed Diboration and Monoboration of 1,3-Dienes (an Alternative Transition-Metal-Free Version Reported in This Work)**




However, the transition-metal-free borylation of 1,3-dienes generates questions about why the conjugated 1,4-hydroboration might be favored versus 1,2-diboration in the transition-metal-free context, as well as whether the *E*- or the *Z*-allyl boronate products are going to be preferentially formed in noncyclic systems.

In order to answer all of the questions raised above, we selected the model substrate *trans*-1-phenyl-1,3-butadiene (**1**) and we carried out the borylation with 1.1 equiv of $B_2pin_2$ in the presence of 15 mol % of $Na_2CO_3$ and MeOH as solvent (1 mL) at 90 °C. The analysis of the unpurified reaction mixture by $^1$H NMR spectroscopy established 47% conversion toward the 1,4-hydroborated product **2** (*E*/*Z* = 2/1) (Scheme 2, top) and 22% of polyborylated products[12] without the consumption of all the starting material. Decreasing the temperature to 70 °C and increasing the amount of base to 30 mol % allowed the formation of **2** in 60% (*E*/*Z* = 3/1), minimizing the byproduct formation. Remarkably, this is the first attempt to borylate 1,3-

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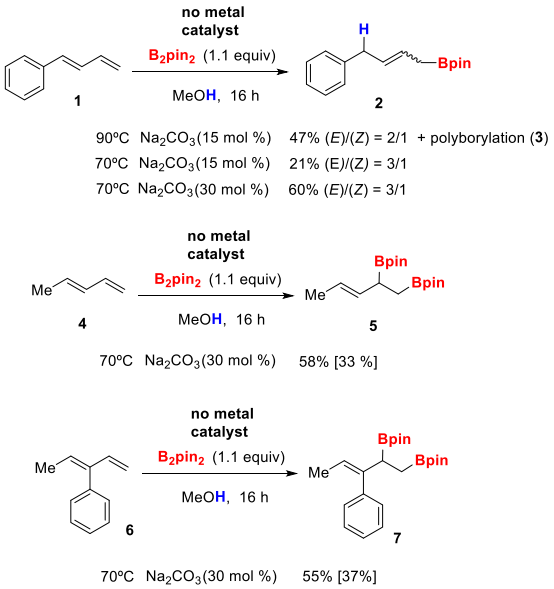
**Scheme 2. Transition-Metal-Free 1,4-Hydroboration of *trans*-1-Phenyl-1,3-butadiene (1) and 1,2-Diboration of *trans*-1-Methyl-1,3-butadiene (4) and (*Z*)-Penta-1,3-dien-3-ylbenzene (6)[a]**

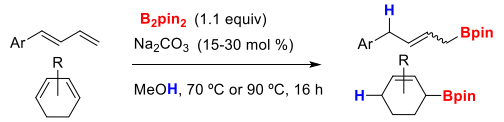


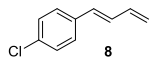
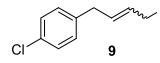
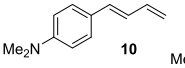
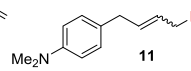
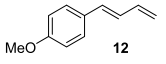
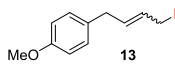
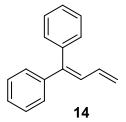
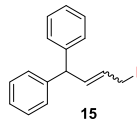
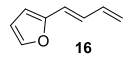
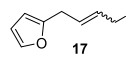
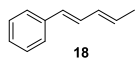
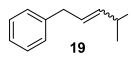
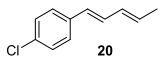
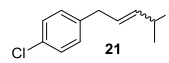
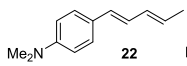
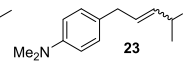
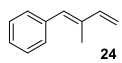
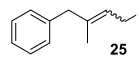
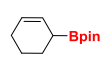
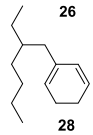
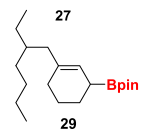
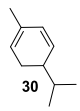
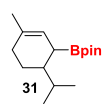

[a]Percent NMR yields calculated in $^1$H NMR spectra with naphthalene as internal standard (% isolated yields).

dienes in a transition-metal-free context, and the results seem to be complementary to Huang and co-workers' work,[13] where the same substrate **1** underwent 1,4-hydroboration with HBpin in the presence of iminopyridine Fe complexes, but forming principally the secondary (*Z*)-allylboronate. When *trans*-1-methyl-1,3-butadiene (**4**) reacted with 1.1 equiv of $B_2pin_2$, 1,2-diboration of the terminal alkene took place instead to form product **5** in 58% NMR yield (33% isolated) (Scheme 2). It seems that the competing 1,2-diboration is favored versus 1,4-hydroboration for alkyl substituents at the $C_1$ position,[14,15] in contrast to the Fe−Mg-catalyzed 1,4-hydroboration of 1-alkyl-substituted 1,3-dienes or 2-alkyl-substituted 1,3-dienes, observed by the groups of Huang and Ritter, respectively.[13,16] To confirm the previous observation, we conducted the transition-metal free borylation of (*Z*)-penta-1,3-dien-3-ylbenzene (**6**), and as expected, the 1,2-diborated product **7** was also formed despite the presence of the phenyl group at the $C_2$ position (Scheme 2).

To extend the conjugative borylation on *trans*-1-aryl-1,3-butadiene type substrates, we carried out a systematic study with the optimized reaction conditions based on the addition of $B_2pin_2$ (1.1 equiv) to a solution of MeOH that contains the substrate and 30 mol % of $Na_2CO_3$. As can be seen in Table 1, *trans*-1-aryl-1,3-butadienes that contain electron-donating and electron-withdrawing substituents on the aryl group do not affect the reaction outcome (Table 1, entries 1−3). However, a slight increase in the *E*/*Z* ratio up to 4/1 was observed for product **13**. It is worth mentioning that substrate buta-1,3-diene-1,1-diyldibenzene **14** was borylated with similar success but the enhanced *E*/*Z* ratio (up to 9/1) indicated the preference for the *E* isomer in compound **15** when the two aryl groups are located at the terminal position (Table 1, entry 4). We were also able to conduct the transition-metal-free 1,4-hydroboration of (*E*)-2-(buta-1,3-dien-1-yl)furan **16** toward the desired allyl boronate product **17**, demonstrating the

**Table 1. Transition-Metal-Free 1,4-Hydroboration of *trans*-1-Aryl-1,3-butadienes[a]**




| entry | substrate | product | *E*/*Z* | %NMRYield[b] [%I.Y.] |
|---|---|---|---|---|
| 1 |  **8** |  **9** | 3/1 | 50 [23] |
| 2 |  **10** |  **11** | 3/1 | 55 [38] |
| 3 |  **12** |  **13** | 4/1 | 61 [32] |
| 4 |  **14** |  **15** | 9/1 | 62 [40] |
| 5 |  **16** |  **17** | 4/1 | 53 [15] |
| 6 |  **18** |  **19** | 3/1 | 71 [16] |
| 7 |  **20** |  **21** | 3/1 | 50 [23] |
| 8 |  **22** |  **23** | 3/1 | 55 [38] |
| 9 |  **24** |  **25** | 3/1 | 65 [60] |
| 10[c] |  **26** |  **27** | | 55 [35.5] |
| 11[c] |  **28** |  **29** | | 79 [59] |
| 12[c] |  **30** |  **31** | | 65 [59] |

[a]Reaction conditions: substrate (0.2 mmol), $B_2pin_2$ (1.1 equiv) $Na_2CO_3$ (30 mol %), MeOH (1 mL), 70 °C, 16 h. [b]NMR yields calculated in $^1$H NMR spectra with naphthalene as internal standard (percent isolated yields). [c]$Na_2CO_3$ (15 mol %), 90 °C.

compatibility with other conjugated systems (Table 1, entry 5). The general method was also applied to internal 1,3 dienes such as ((1*E*,3*E*)-penta-1,3-dien-1-yl)benzene **18** and related substrates **20** and **22**. To our delight, the 1,4-hydroboration took place toward the formation of the desired allylic boronates **19**, **21**, and **23** without any reduction in the yield or the *E*/*Z* ratio (Table 1, entries 6−8). The internal substitution in substrate (*E*)-(2-methylbuta-1,3-dien-1-yl)-benzene **24**, also proved not to be influential to the reaction outcome as product **25** was formed with similar conversion and selectivity (Table 1, entry 9).



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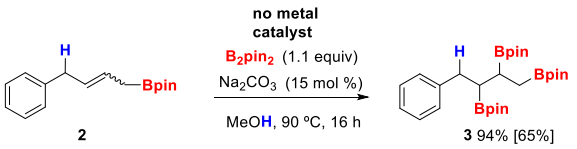
We next considered the possibility to extend the transition-metal-free allylic borylation methodology to cyclic 1,3-dienes. We found that cyclohexadiene (**26**) was transformed into the corresponding allyl boronate via 1,4-hydroboration under the same reaction conditions as for non-cyclic systems except that 90 °C was required (Table 1, entry 10). This is interesting because in this substrate there are no aryl substituents that direct the conjugative borylation as in substrate **2**, and so the 1,2 diborated product could be expected to form as in the borylation of *trans*-1-methyl-1,3-butadiene (**4**) (see Scheme 2). In extension, substrate 2-(2-ethylhexyl)cyclohexa-1,3-diene (**28**) could be efficiently borylated toward the allylic bororonate product **29**, despite the added steric hindrance provided by having a substituent in the internal position (Table 1, entry 11). Even the disubstituted cyclic 1,3-diene 5-isopropyl-2-methylcyclohexa-1,3-diene (**30**) was transformed into the allylic boronate product **31**, with an *anti*-configuration of the Bpin moiety in relation to the isopropyl functional group (Table 1, entry 12).

Allyl boronate products are very important building blocks,[17] and in our hands, the allyl boronate product **2** has been transformed into 1,2,3-triborated product **3** via consecutive transition-metal-free diboration of the internal double bond (Scheme 3). The triborated product **3** was

**Scheme 3. Synthesis of 1,2,3-Triborated Products from the Allyl Boronates**

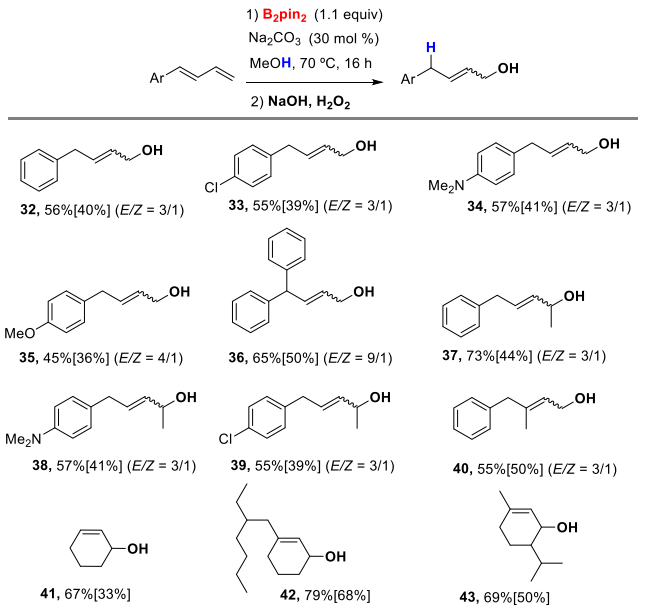



quantitatively formed and isolated from the reaction as a unique product. The extension of this interesting transformation has been recently explored with a detailed study of the concomitant selective cross-coupling reaction from triborated compounds.[12] The in situ oxidative workup of the allyl boronate compounds prepared in this work provide the corresponding allylic alcohols in a transition metal-free context with a preference for the *E*-isomer (Scheme 4). The formation of allylic alcohols through borylation reactions was recently observed in the Cu-catalyzed borylation of vinyl cyclic carbonates via an $S_N2'$ mechanism, also with preference on the *E* isomer.[18]

A proposed reaction mechanism for the transition-metal-free borylation of 1,3-dienes may involve first activation of the $B_2pin_2$ with MeOH/base to form adduct [MeO-Bpin-Bpin]$^-$[Hbase]$^+$ followed by nucleophilic attack of the Bpin($sp^2$) moiety to the terminal double bond (Figure 1). The conjugative borylation may generate two isomeric allylic anion intermediates that can be protonated with MeOH used as solvent.

We performed DFT studies[19] on the mechanism depicted in Figure 1 in order to understand the stereo- and regioselectivity in the transition-metal-free borylation of cyclic and 1-aryl-substituted 1,3-dienes. Previous computational studies have demonstrated the nucleophilic character of the $sp^2$ boron moiety[20] in the acid−base Lewis adduct [MeO-Bpin-Bpin]$^-$[Hbase]$^+$ and that the electron-withdrawing substituents can favor the hydroboration over the diboration of C=C double bonds by stabilizing the anionic monoborylated

**Scheme 4. Transition-Metal-Free 1,4-Hydroboration/Oxidation of *trans*-1-Aryl-1,3-butadienes**



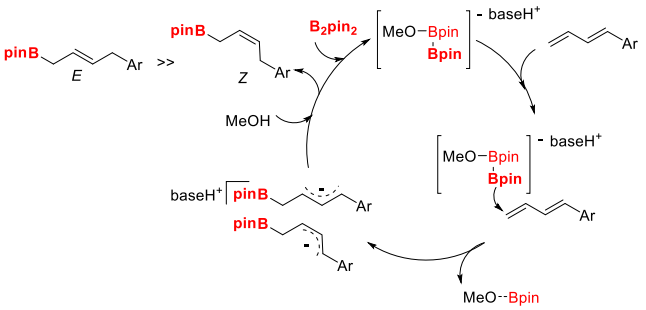




**Figure 1.** Proposed mechanism for transition-metal-free borylation of 1,3-dienes.

intermediate.[21] Figure 2 displays the computed potential free-energy profile for the 1,4-hydroboration of 1-*trans*-phenylbutadiene (**1**) to yield both the *E* and the *Z* stereoisomeric products. The calculated free-energy barrier for the initial nuclophilic Bpin transfer to the terminal carbon of diene **1** is moderate (24.5 kcal·mol$^{-1}$) and leads to a stable anionic intermediate **I1**-*E* (*E*-path, solid lines). Similar to that observed for allenamides,[22] the anionic, 3-membered boracycle intermediate opens to form a more stable allylic anion with an alkyl boronate group attached to the terminal carbon. Subsequent protonation of **I1**-*E* leads to the hydroborated product. The observed regioselective protonation of $C_1$ can be rationalized from the charge distribution in the allylic intermediate **I1**-*E* (Figure 2). Our calculations show that the phenyl-substituted $C_1$, supports a larger negative charge than the allylic $C_2$ and $C_3$. Consequently, the $C_1$ carbon should be more reactive toward protonation in agreement with the observed preference for 1,4- over the 3,4-hydroboration. In line with this, the estimated barrier for protonation at $C_1$ using a single MeOH solvent molecule is quite low (5.1 kcal·mol$^{-1}$).

To explain the formation of the observed *Z* product, the *E* path has to undergo an isomerization process at some point in the catalytic cycle. The isomerization of the allylic intermediate **I1**-*E* to **I1**-*Z* via rotation around the $C_2-C_3$ bond is unlikely because the computed barrier of 19.3 kcal·mol$^{-1}$ is significantly



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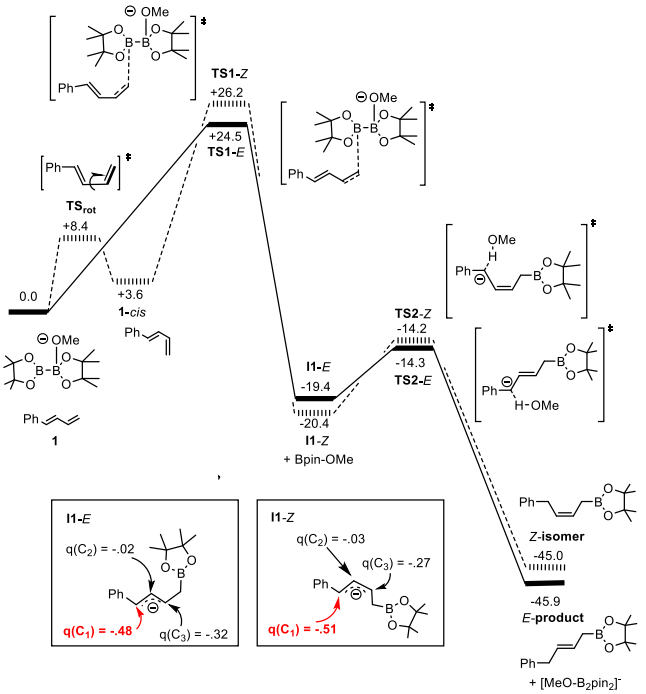


**Figure 2.** Potential free-energy profiles (kcal·mol$^{-1}$) for the 1,4-hydroboration of 1-*trans*-phenyl-1,3-butadiene (**1**) by $B_2pin_2$ in MeOH/base. Solid and dashed lines correspond to the paths yielding the *E* and *Z* stereoisomeric products.

higher than that for the forward protonation reaction (5.1 kcal·mol$^{-1}$). Instead, we propose that the *trans* diene isomerizes to the *cis* conformation. The computed barrier (8.4 kcal·mol$^{-1}$) and the energy difference (+3.6 kcal·mol$^{-1}$) might allow it. Borylation of the *cis* conformer yields intermediate **I1**-*Z* with the alkyl boronate group *cis* to $C_1$ (dashed lines in Figure 2). The lower stability of the *cis* isomer is partially compensated by a lower free-energy barrier for borylation (22.6 vs 24.5 kcal·mol$^{-1}$). Interestingly, the higher reactivity of *cis* conformations of *α,β*-unsaturated aldehydes and ketones has been explained from secondary orbital interactions which allow a better stabilization of the developing negative charge.[23] Overall, the transition state for the *Z* path (**TS1**-*Z*) is only 1.7 kcal·mol$^{-1}$ higher than the corresponding transition state for the *E* path (**TS1**-*E*). This results in a small preference for the *E* over the *Z* products, in full agreement with experimental observations.

For cyclic 1,3-dienes, we propose the same type of mechanism, in which only the *Z*-path is possible due to the *cis* configuration of the diene (Figure 3). The computed barrier for the nucleophilic Bpin transfer to the cyclohexadiene **26** is somewhat larger (27.4 kcal·mol$^{-1}$) than that for 1-*trans*-phenylbutadiene (24.5 kcal·mol$^{-1}$) but still reasonable for a reaction occurring at 90 °C. In this case, the absence of the phenyl substituent yields a less stable allylic anion intermediate **I1c** and makes possible the formation of the boracyclic species **I′c**. These intermediates, **I1c** and **I′c**, are close in energy and interconvert easily. In line with the observed regioselectivity toward 1,4-hydroboration, the $C_1$ carbon of both species supports the largest negative charge favoring its protonation, for which we found very small electronic energy barriers (<1 kcal·mol$^{-1}$).

It can be concluded that transition-metal-free borylation of 1,3-dienes takes place through $S_N2'$-type mechanisms with a preference for the *E* stereoisomeric allylic boronate product

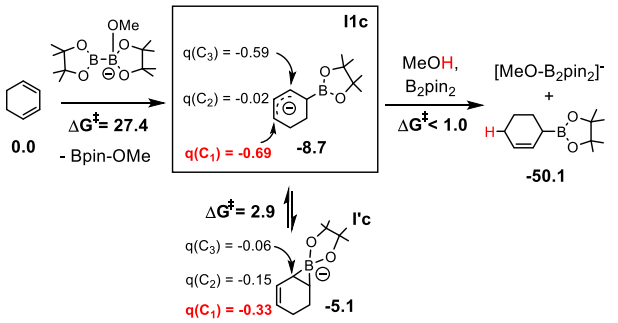


**Figure 3.** Proposed reaction mechanism for the 1,4-hydroboration of cyclohexadiene by $B_2pin_2$ in MeOH/base. Relative free-energies and barriers in kcal·mol$^{-1}$.

formation. 1,4-Hydroborations are favored versus 1,2-diboration for 1-*trans*-arylbutadienes. Computational studies identify the key steps in the transition-metal-free conjugative borylation that rationalize the preference for 1,4-hydroborated products as well as the *E* stereoisomerism in the allylic boronate products.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00531.

Experimental procedures and spectral data, $^1$H, $^{13}$C, and $^{11}$B spectral images, and computational studies (PDF)

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### Notes

The authors declare no competing financial interest.

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