

The Effect of Carborane Substituents on the Lewis Acidity of Boranes

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ABSTRACT

The Lewis acidity of primary, secondary, and tertiary boranes with phenyl, pentafluorophenyl, and all three isomers of icosahedral carboranes (*ortho*, *meta*, and *para*) were investigated by computing their fluoride, hydride, and ammonia affinities as well as global electrophilicity indices and LUMO energies. From these calculations, the substituent effects on the Lewis acidity follow the trend of *ortho*-carborane > *meta*-carborane > *para*-carborane > C₆F₅ > C₆H₅.

INTRODUCTION

Boranes are classical Lewis acids that are widely used due to their electron deficiency and desire to fill the vacant p-orbital to satisfy its octet.¹⁻⁶ The substituents bound to the boron center greatly influence the accessibility and energy of the empty p-orbital providing a handle to tune the Lewis acidity and steric profile.⁷ The application of trihalo- and trialkyl- boranes in catalysis is limited in comparison to triaryl- species.^{8,9} While trihaloboranes are generally the most Lewis acidic,⁷ the B–X bonds are reactive with many functional groups and difficult to manipulate due to moisture-sensitivity and volatility, thus not useful for many applications. The trialkylboranes are the least Lewis acidic and modifying the groups on the alkyl chain only results in small permutations in the acid strength, making them challenging to tune, and only weak Lewis acids. Triarylboranes have garnered the greatest interest owing to their exceptional stability as well as the ability to fine-tune their Lewis acidity by modification of the substituents on the aryl group.^{8,9} Electron-withdrawing groups such as –F, –Cl, and –CF₃ can be installed to increase the Lewis acidity at the boron center.¹⁰⁻²⁰ The perfluorinated triarylborane, tris(pentafluorophenyl)borane [B(C₆F₅)₃],²⁰ has found the most extensive applications in Lewis acid mediated chemistry, notably in catalysis, olefin polymerization, and as the Lewis acid component in frustrated Lewis pairs.^{9, 21-29} Fluoroarylboranes with a *para*-fluorine atom can be susceptible to deleterious reactivity via nucleophilic substitution at that position that limits their use.^{30, 31} Beyond fluorinated arene substituted boranes, little research has been directed to find new Lewis acids with similar, or better, catalytic activity. Exotic means have emerged that include cationic substituents and functional groups that chelate metals to serve as electron-withdrawing groups.^{32-41,42-45} The cationic substituents and metals can be reactive themselves rather than behave as spectator ligands.

Berionni and coworkers have been leveraging constrained geometry at the boron center to generate extremely Lewis acidic boranes in situ, but the free Lewis acids have yet to be isolated.⁴⁶⁻⁴⁸

Dicarbadoecaboranes, or carboranes, are $C_2B_{10}H_{12}$ icosahedral clusters composed of boron, carbon, and hydrogen atoms that are bonded non-classically.⁴⁹ The three isomers of neutral $C_2B_{10}H_{12}$ are named based on the relative positions of the two carbon atoms in the icosahedron: *ortho* (carbon atoms adjacent, 1- and 2-positions), *meta* (carbon atoms separated by a boron atom, 1- and 7-positions), and *para* (carbon atoms separated by two boron atoms on opposite sides of the cage, 1- and 12-positions).⁴⁹ The molecular orbital diagrams of the C_2B_{10} cages in all isomers have all 13 cluster bonding orbitals fully occupied and the antibonding orbitals unoccupied leading to high kinetic stability. Icosahedral carboranes are often termed as three-dimensional aromatics due to the high delocalization of the electron density throughout the cluster. Since their disclosure in the 1960s, carboranes have been explored in many fields of chemistry including medicine, catalysis, polymers, optoelectronic applications, and the metal-ion extraction of nuclear waste.⁵⁰⁻

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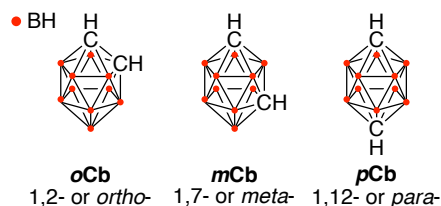


Figure 1: *closo*- $C_2B_{10}H_{12}$ Carborane isomers.

The research groups of Lee and Park prepared aryl boranes that featured *ortho*-carboran-1-yl groups on the *para*- and *meta*- positions of the aryl groups.⁵⁴⁻⁵⁸ Fluoride binding was enhanced by three orders of magnitude with one carborane-substituted arene on boron and four orders of magnitude when three carborane-substituted arenes were on boron in comparison to species

lacking carboranes. The *o*-carborane-functionalized aryl boranes demonstrate C-bound *o*-carborane serves as effective electron-withdrawing group, but it is more effective to directly bind it to boron rather than having an arene spacer.⁵⁹⁻⁶² Fox and coworkers prepared C-dimesitylboryl-*o*-carboranes (**1** and **2**) and calculated their fluoride ion affinities to be 132.9 and 127.3 kcal/mol, respectively, which exceed that of the arene bridged species (123.9 and 122.6 kcal/mol, respectively).⁶³ Welch and co-workers prepared a derivative of **1** and **2** with a methyl group on the other carbon (**3**) that exhibited similar Lewis acidity.⁶⁴ Marder and co-workers synthesized a bis(*o*-carboranyl)-(*p*-tolyl)-borane **4**, that could be reduced and isolated as the corresponding radical anion attributed to its low energy LUMO.⁶⁵

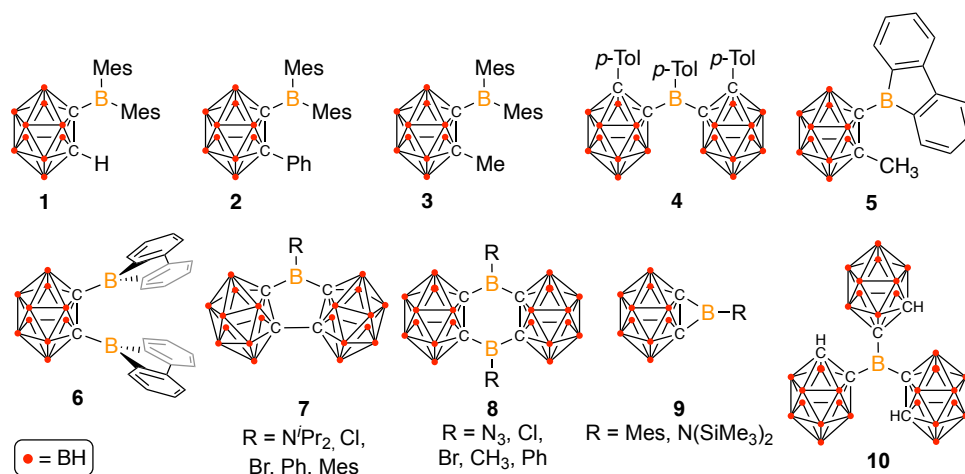


Figure 2: Known carborane substituted boranes with measured Lewis acidity.

Marder, Braunschweig, and coworkers reported the mono- and bis-boraffluorene *o*-carboranyl species **5** and **6**,^{66, 67} that are both susceptible to endocyclic B–C bond cleavage or insertion to access heterocycles,⁶⁸ in many cases similar to 9-boraffluorenes with B-aryl or B-halo substitution.⁶⁹⁻⁸² Carboranes are considered 3D analogues of benzene and accordingly, carborane containing analogues of fluorene and anthracene have been targeted. Ye,⁸³ Dobrovetsky,⁸⁴ and our

group⁸⁵ reported bis-*ortho*-carboranyl-borane analogues of a 9-borafluorene with various substitution on boron (**7**). The diisopropylamino species and mesityl were not Lewis superacids due to π -donation and bulk, respectively but Br, Cl, Ph were all classified as Lewis superacids (LSAs). A LSA is a species with a theoretically calculated fluoride ion affinity (FIA) exceeding SbF_5 .^{86, 87} Ye and coworkers have prepared analogues of anthracene in which the two phenyl groups are replaced by *o*-carboranes (**8**).^{88, 89} Both the calculated hydride and fluoride ion affinities (HIA and FIA) follow the Lewis acidity trend of $\text{Br} > \text{Cl} > \text{Ph} > \text{N}_3 > \text{CH}_3$ with all five species exceeding the HIA of $\text{B}(\text{C}_6\text{F}_5)_3$ and the FIA of SbF_5 . The boracyclic analogues of the cyclopropenium cation were also prepared featuring the two carbon atoms of *o*-carborane (**9**).^{90, 91} Amino substituents as π -donors or bulky mesityl groups were required to isolate these species due to the reactivity of the strained three-membered ring.

Our team recently prepared tris(*o*-carboranyl)borane (**10**) that is a Lewis superacid that promotes catalytic C–F bond functionalization reactions.⁹² The aforementioned studies clearly indicate the ability of the *o*-carboranes to act as an electron-withdrawing moiety, but the relative Lewis acidic properties are not clearly evaluated nor do any examples with the other carborane isomers exist. In this work, we examine the electron-withdrawing effect of all three carborane isomers on the Lewis acidity of boranes.

RESULTS AND DISCUSSION

To analyze the carborane substituent effects on Lewis acidity, three sets of compounds will be investigated, H_2BR , HBR_2 , and BR_3 complexes where R is an *ortho*-, *para*-, or *meta*-carborane (*o*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, *p*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, and *m*- $\text{C}_2\text{B}_{10}\text{H}_{11}$, respectively). The only known compounds in these are the

homoleptic tris(*ortho*-carboranyl)borane **10** and a secondary borane $\text{HB}(o\text{-CH}_3\text{-C}_2\text{B}_{10}\text{H}_{10})_2$, where for the latter the *ortho*-carbon bears C–CH₃ rather than C–H.^{92,93} The results will be compared to the phenyl and pentafluorophenyl substituted variants. The computational methods used to assess Lewis acidity are Hydride, fluoride, and ammonia affinity calculations, the global electrophilicity index (GEI), and LUMO energy levels. Fluoride and hydride ions exhibit high basicity and are small in size, and thus, steric effects are minimized. Stephan and coworkers recently developed the GEI that calculates the ability of a Lewis acid to accept a single electron which is advantageous in some aspects, as it reduces the structural reorganization in comparison to the coordination of an atom or ion and is not influenced by the hardness of the base.⁹⁴

For H₂BR molecules, there is a substantial effect on the hydride and fluoride affinities for changing the position of the relatively electron withdrawing C–H carborane cage substituent from the *ortho*- to the *meta*- position with a drop of nearly 30 kJ/mol. There is a smaller decrease in the ammonia affinity as well. The same effect is seen as the C–H is moved to the *para*- position, albeit with less magnitude with a further drop in 10 kJ/mol for fluoride and hydride affinities and a slight decrease in the ammonia affinity. Substituting the C–H for a C–CH₃ group on the carborane cage has a minimal effect, slightly reducing the Lewis acidity which is in line with the inductive effect of –CH₃ on carbon. In all cases the Lewis acidity is significantly higher than the corresponding –C₆H₅ or –C₆F₅ substituted systems. The LUMO energies and GEIs follow the same trend with the LUMO increasing in energy as the C–H becomes more distant from the central boron. The LUMO of the –C₆F₅ substituted H₂BR is lower in energy than the carborane substituted species, however, it is more delocalized with contribution on the –C₆F₅ ring, whereas the carborane substituted species have the LUMO entirely localized on B as previously determined for the isolated tris(*ortho*-carboranyl)borane (**10**).

Table 1: Calculated values of H₂BR model complexes. HIA = hydride ion affinity, FIA = fluoride ion affinity, all affinities are in kJ/mol; GEI = global electrophilicity index; %V_{Bur} = Lewis acid buried volume (%).

R	HIA	FIA	NH ₃ Affinity	LUMO (eV)	GEI	%V _{Bur}
<i>o</i> -C ₂ B ₁₀ H ₁₁	482	464	119	-2.81	2.82	41.1
<i>o</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	482	465	117	-2.77	2.77	44.8
<i>m</i> -C ₂ B ₁₀ H ₁₁	451	437	112	-2.53	2.56	41.9
<i>m</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	448	434	111	-2.48	2.51	41.9
<i>p</i> -C ₂ B ₁₀ H ₁₁	441	427	110	-2.44	2.49	41.7
<i>p</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	434	421	104	-2.37	2.43	41.7
C ₆ H ₅	354	326	61	-2.24	2.24	34.2
C ₆ F ₅	415	383	90	-3.02	3.07	37.5

The steric implications of changing a -H to -CH₃ at the carbon atoms of each isomer were considered using the method of determining Lewis acid buried volume developed by Radius and co-workers using the SambVca 2.1 tool on the respective fluoride adducts. The C-H and C-CH₃ carborane substituted boranes are more sterically protected at boron than -C₆F₅ and -C₆H₅ in all cases. The steric effect at boron for C-CH₃ rather than C-H is only impactful on the *ortho*-substituted carborane species with no change found if methyl substitution is at the *meta*- or *para*-positions.

We recently reported HB(*o*-CH₃-C₂B₁₀H₁₀)₂, the carborane analogue of Piers' borane [HB(C₆F₅)₂],⁹⁵⁻⁹⁷ with C-CH₃ substituents on the *ortho*-carbon positions of the carborane cages. Here, the other possible isomers/analogues are considered. In all cases a substantial increase in Lewis acidity towards hydride and fluoride is calculated in the secondary borane over the primary boranes. The ammonia affinities are less affected and even decrease slightly. There is a lowering of the LUMO energies and corresponding increase in the GEIs as compared with the H₂BR species. With two carboranes the effect on the hydride and fluoride affinities changing from *ortho*- to *meta*- to *para*-positioning of the C-H has an increased effect, dropping affinities by approximately 50 kJ/mol

from *ortho*- to *meta*-, as compared with approximately 30 kJ/mol for the same change with H₂BR. As with H₂BR there is a lessened effect changing *meta*- to *para*-, albeit still increased with a drop of around 20 kJ/mol in this case. In line with H₂BR species, all carborane substituted analogues have greater Lewis acidity than –C₆H₅ or –C₆F₅ substitution.

Table 2: Calculated values of HBR₂ model complexes. All affinities are in kJ/mol. %V_{Bur} = Lewis acid buried volume (%).

R	HIA	FIA	NH ₃ Affinity	LUMO (eV)	GEI	%V _{Bur}
<i>o</i> -C ₂ B ₁₀ H ₁₁	549	542	118	-3.33	3.24	57.1
<i>o</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	540	527	120	-3.10	3.10	64.7
<i>m</i> -C ₂ B ₁₀ H ₁₁	498	489	109	-2.75	2.76	58.0
<i>m</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	494	485	113	-2.66	2.68	58.0
<i>p</i> -C ₂ B ₁₀ H ₁₁	482	469	106	-2.59	2.61	58.0
<i>p</i> -CH ₃ -C ₂ B ₁₀ H ₁₀	479	465	101	-2.43	2.47	57.9
C ₆ H ₅	358	351	44	-2.19	2.20	44.3
C ₆ F ₅	457	429	100	-3.26	3.40	47.0

With two carboranes on boron, changing C–H to C–CH₃ at the *ortho*- position has a significant impact on the Lewis acid buried volume at the central boron with an increase from 57.1% to 64.7%. If the C–H is at the *meta*- or *para*-position, as with H₂BR changing to C–CH₃, there is no impact on the Lewis acid buried volume at the central boron, with Lewis acid buried volume at 58% in all cases.

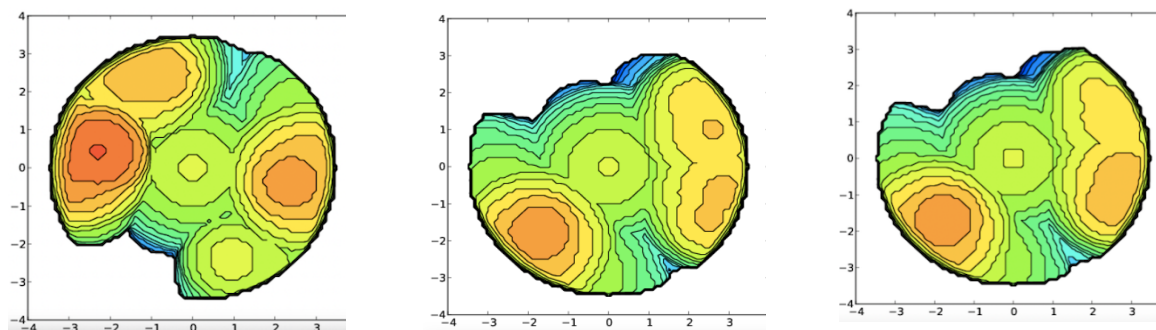


Figure 3. Lewis acid % buried volume plots for $\text{HB}(o\text{-CH}_3\text{-C}_2\text{B}_{10}\text{H}_{10})_2$, $\text{HB}(m\text{-CH}_3\text{-C}_2\text{B}_{10}\text{H}_{10})_2$, $\text{HB}(p\text{-CH}_3\text{-C}_2\text{B}_{10}\text{H}_{10})_2$ (left to right, respectively).

In the secondary boranes, the steric imposition of the carborane notably affects the C–B–C bond angles more so than the $-\text{C}_6\text{F}_5$ and $-\text{C}_6\text{H}_5$ substituents. For the BR_3 and H_2BR compounds, the bond angles are exactly or nearly 120° . For secondary boranes, the $-\text{C}_6\text{F}_5$ and $-\text{C}_6\text{H}_5$ substituted species have C–B–C bond angles of $125\text{--}126^\circ$, but for the carborane variants they are more obtuse at $128\text{--}129^\circ$. Surprisingly, installing methyl groups, regardless of the isomer, has a negligible effect on the bond angle presumably due to the ability of the icosahedron to rotate with the small H substituent.

For BR_3 only C–H carboranes were evaluated as changing C–H to C– CH_3 has only meager effects on the Lewis acidity in the primary and secondary borane systems. Hydride and fluoride ion affinities are higher for BR_3 than the other HBR_2 and H_2BR sets of compounds considered, with a maximum at **10**. This is exemplified in the graphs in figure 3. Hydride and fluoride affinities drop approximately 70 kJ/mol upon changing the isomer from *ortho*- to *meta*- and reduce by 24 kJ/mol from *meta*- to *para*- in the BR_3 systems. Notably, the fluoride ion affinity for a Lewis superacid is set at the value for SbF_5 at 493 kJ/mol , meaning all three carborane substituted BR_3 species are Lewis superacids while the *ortho*-carboranyl substituted secondary borane is the only Lewis

superacid in that class. This data indicates that there is a general additive effect in increasing the number of carborane substituents on the fluoride and hydride affinities. The general trend for LUMO energy level also follows this. For the ammonia affinity, there is less of a trend with them being less variable in adding more substituents. Compound **10** is the bulkiest trisubstituted borane reported to date and moving the C–H position to *meta*- or *para*- increases the Lewis acid buried volume % at boron even more owing to the slightly longer B–H adjacent to the central boron as compared to C–H. If these derivatives could be synthesized it would represent a new limit for steric congestion at a boron Lewis acid.

Table 3: Calculated values of BR₃ complexes. All affinities are in kJ/mol. %V_{Bur} = Lewis acid buried volume (%).

R	HIA	FIA	NH ₃ Affinity	LUMO (eV)	GEI	%V _{Bur}
<i>o</i> -C ₂ B ₁₀ H ₁₁	622	605	149	−3.99	4.22	71.9
<i>m</i> -C ₂ B ₁₀ H ₁₁	551	538	102	−3.28	3.32	73.4
<i>p</i> -C ₂ B ₁₀ H ₁₁	527	514	96	−3.08	3.09	73.6
C ₆ H ₅	356	356	30	−2.09	2.11	53.1
C ₆ F ₅	484	452	97	−3.50	3.78	58.9

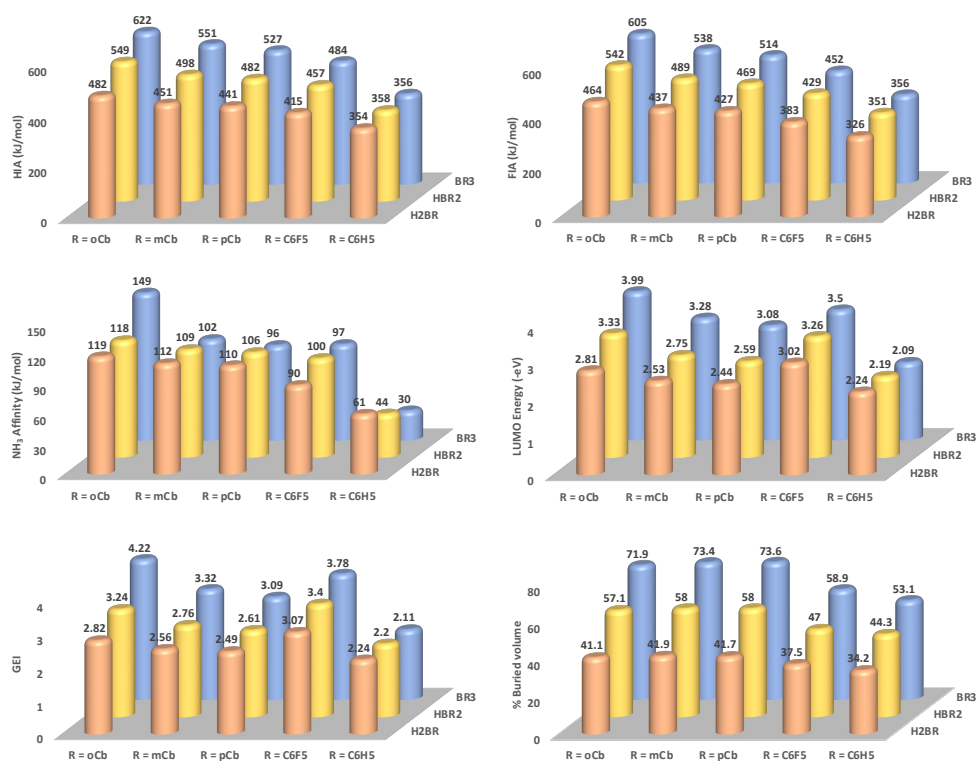


Figure 4: Fluoride ion affinity (FIA), hydride ion affinity (HIA), NH₃ affinity, LUMO, GEI, and buried volume (%) graphs of compounds examined.

CONCLUSIONS

This study indicates that all three isomers of carboranes (*ortho*, *meta*, and *para*) are superior substituents for increasing the Lewis acidity of boranes than pentafluorophenyl or phenyl groups. The high fluoride ion affinities comfortably place all three of the homoleptic tris(carborane)boranes in the Lewis superacid regime. While the tris(*ortho*-carboranyl)borane is known, the *para*- and *meta*-variants are not and represent interesting targets. This report establishes carborane-substituted boranes as powerful Lewis acids and offers much needed diversification in the field of boron Lewis acids. Although fluorinated arene-substituents are effective, their planar

steric profile is very different than the three-dimensional profile of the boranes. In addition, the bulk in these carborane Lewis acids should make them effective as components in frustrated Lewis pair chemistry.

COMPUTATIONAL METHODS

Calculations were performed using Gaussian 16.⁹⁸ Coordinates and electronic energies are given for BP86/SV(P) geometry optimizations and single point vibrational frequency calculations.⁹⁹⁻¹⁰² Fluoride and hydride affinities were calculated using Krossing's method using an isodesmic comparison to the fluoride and hydride affinity of $[\text{CH}_3)_3\text{-Si}]^+$.¹² Ammonia affinities were calculated using B3LYP-D3/def2SVP.^{98,103-105} The molecular orbitals were calculated using B3LYP/def2TZVP and Global Electrophilicity Indices calculated based on the method from Stephan and co-workers.^{106, 107} Lewis acid % buried volume calculations were performed using the SambVca method on .xyz files from the fluoride adducts using BP86/SV(P) geometry optimizations as per the method from Radius and co-workers.^{108, 109} The F atom was selected as the centre of the sphere, Z defined by B, the xy plane defined by a carbon bound to boron and then the F atom omitted.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Cartesian coordinates of optimized geometries in .xyz format

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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