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## ARTICLE

Oxidation-Induced Nucleophilic Substitution at Electron-Rich B(12) Vertex in  $[\text{CB}_{11}\text{H}_{12}]^-$  under Catalyst-Free ConditionsWanqi Sun,<sup>a,d</sup> Yujie Jin,<sup>a,b,d</sup> Yongtao Wang,<sup>\*a,b</sup> Zeyu Wen,<sup>a</sup> Jizeng Sun,<sup>a</sup> Jia Yao,<sup>a,b</sup> Simon Duttwyler,<sup>a</sup> Haoran Li<sup>\*a,b,c</sup>Received 00th January 20xx,  
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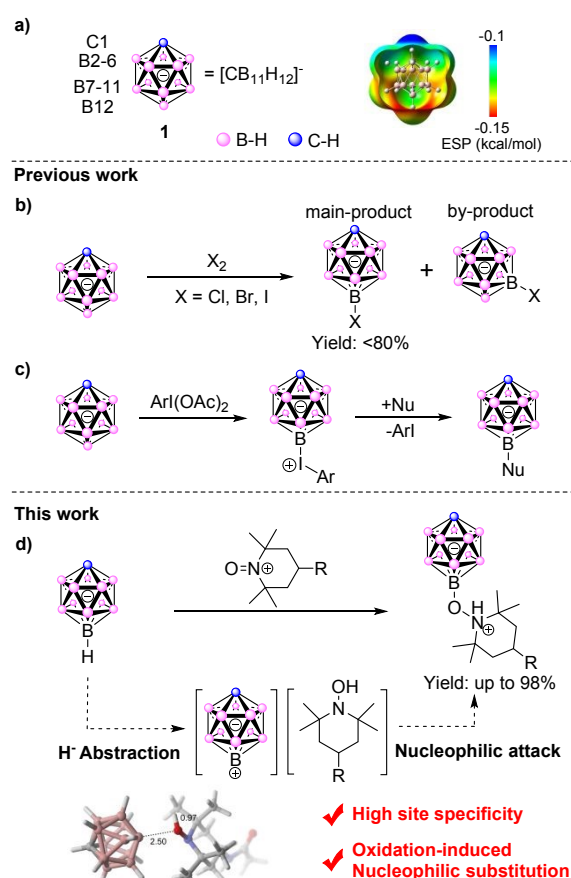
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Highly regioselective B(12) substitutions of the monocarborane anion  $[\text{CB}_{11}\text{H}_{12}]^-$  has been a challenge. Here, we synthesized a stable B–O–N zwitterionic compound with an impressively yield (isolated yield up to 98%) and excellent regioselectivity at the B(12) position under catalyst-free conditions. The kinetics, substituent effect, and capture experiments are paired with theoretical calculations, showing that the reaction mechanism is oxidation-induced nucleophilic substitution. The hydride anion at the B(12) position is abstracted by oxoammonium oxidant with favorable energy (the  $\Delta\Delta G^\ddagger$  was 4.2 kcal/mol favored to the *meta*-B–H bonds), thereby changing the electronegativity upon the conversion of  $[\text{CB}_{11}\text{H}_{12}]^-$  to neutral  $[\text{CB}_{11}\text{H}_{11}]$ , in turn giving very high regioselectivity for nucleophilic substitution. This work presents an effective method for synthesizing B(12) oxygen derivatives of the  $[\text{CB}_{11}\text{H}_{12}]^-$  anion.

## Introduction

12-Vertex boron clusters, characterized by their distinctive icosahedral geometry and exceptional stability,<sup>1–4</sup> have garnered significant attention across diverse fields.<sup>5–14</sup> Monocarboranes anion  $[\text{CB}_{11}\text{H}_{12}]^-$ , with single negative charge, have received particular attention.<sup>15–18</sup> Highly regioselective B(12) substitutions are a challenge due to the minimal polarization and high symmetry of the B–H bond.<sup>19–23</sup> Currently, there are two mechanisms for achieving monosubstitution at the B(12) position of  $[\text{CB}_{11}\text{H}_{12}]^-$ : 1) Electrophilic substitution, the electrophilic halogenation is most commonly used.<sup>24–26</sup> However, 7-isomers were always obtained as by-products due to the similar electrostatic potential at B(7–11) to that at B(12) (Fig. 1a). The less regioselective electrophilic substitutions commonly cause lower yields (Fig. 1b); 2) Nucleophilic substitution, boron-centered cations were generally proposed to be key intermediates in the chemistry of polyhedral boron hydrides,<sup>27–29</sup> however, limited works are reported on the functionalization of  $[\text{CB}_{11}\text{H}_{12}]^-$ . Hydroxylation at B(12) position using 80% sulfuric acid yields 12-hydroxy anions under elevated temperatures.<sup>30</sup> Electrophile-induced nucleophilic substitution (EINS)<sup>31</sup> has been proposed for this reaction.<sup>32, 33</sup> Recently, Kaszyński and co-workers found that  $[\text{CB}_{11}\text{H}_{12}]^-$  reacts with iodobenzene diacetate, yielding zwitterionic products Ar–I<sup>+</sup>–

substitution to generate a series of functionalized derivatives of  $[\text{CB}_{11}\text{H}_{12}]^-$  anion (Fig. 1c).<sup>34, 35</sup>



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$[\text{CB}_{11}\text{H}_{11}]^-$  at the B(12) position, which undergo nucleophilic

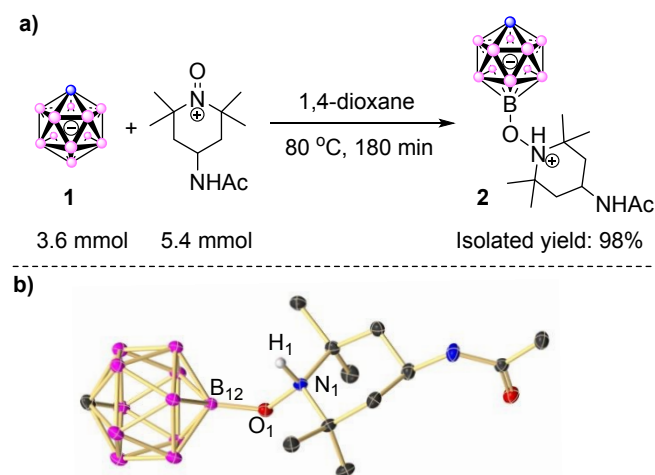


Oxoammonium salts are commonly utilized as oxidants in organic synthesis for their easy access and recyclability,<sup>36–41</sup> and they were commonly used as hydride abstracting reagents.<sup>42, 43</sup> For example, they catalyzed the oxidation of alcohols or ether to yield the corresponding aldehydes, ketones, or carboxylic acids via a hydrogen anion abstraction mechanism.<sup>44</sup> Recently, Lin and co-workers achieved the oxidation of ethers to lactones with oxoammonium cation, where the hydride abstraction from C-H was also suggested.<sup>45</sup>

Inspired by those literature works, we hypothesized that oxoammonium salts might also abstract hydride from B-H bonds in  $[\text{CB}_{11}\text{H}_{12}]^-$ . As expected, we found a novel coupling reaction of oxoammonium salts and  $[\text{CB}_{11}\text{H}_{12}]^-$  to form stable B–O–N compounds under catalyst-free conditions. This approach exhibited excellent regioselectivity with high B(12) substituted products. The reaction mechanism was suggested to undergo an oxoammonium oxidation-induced nucleophilic substitution (OINS) with various mechanistic studies, such as kinetic studies, substituent effects, EPR spectroscopy, trapping experiments, and theoretical calculations.

## Results and discussion

At the very beginning, optimization for the reaction condition was conducted (Table S1). The conditions outlined in entry 12 of Table S1 were identified as optimal. The optimized reaction conditions were  $[\text{CB}_{11}\text{H}_{12}]^-$  with 1.25 equivalents of the commercial agent  $[\text{AcNH-TEMPO}]^+ [\text{BF}_4]^-$  in 1,4-dioxane at 80 °C for 180 min.



**Fig. 2** (a) Gram-scale synthesis and (b) X-ray crystal structures of 2. Cations and H atoms omitted for clarity; 30% displacement ellipsoids.

Under optimal conditions, a scale-up synthesis of 2 was carried out with high isolated yield of 98%. The new compound was characterized through spectroscopic techniques, including  $^1\text{H}$ ,  $^1\text{H}\{^{11}\text{B}\}$ ,  $^{11}\text{B}$ ,  $^{11}\text{B}\{^1\text{H}\}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR, as well as high resolution mass spectrometry (HRMS). The  $^{11}\text{B}$  NMR spectra

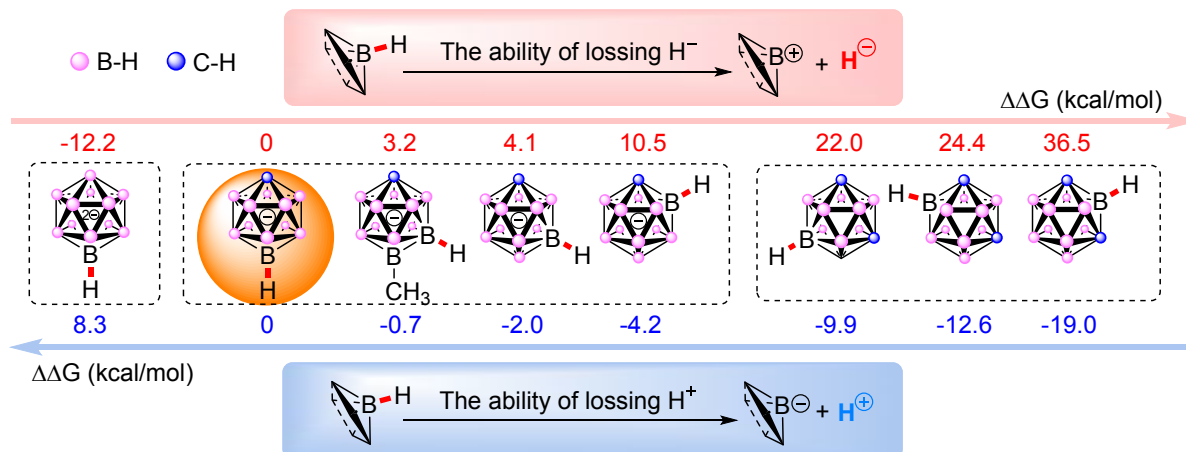
displayed a similar pattern of 1:5:5 with the chemical shifts of B(12) vertices changed from  $\delta = -7.93$  ppm to  $\delta = -11.8$  ppm. Moreover, single crystals of the composition were obtained from an acetone solution via slow evaporation. And the single-crystal X-ray analysis of 2 confirms the molecular structure (Figure 2b). For compound 2, the observed distances are B12–O1 1.459 Å, O1–N1 1.423 Å, with an angle of B12–O1–N1 at 123.33°. The distances and angles are comparable to those reported in previous literature.<sup>46</sup> In addition, the B–O–N compound is zwitterionic compound with high stability.<sup>47, 48</sup> The theoretically calculated dipole moment is 11.75.

In an effort to investigate what the reaction mechanism makes such high regioselectivity, we performed density functional theory (DFT) calculations for heterolytic cleavage of various B–H bonds in  $[\text{CB}_{11}\text{H}_{12}]^-$ . Due to the influence of  $\text{H}^+$  or  $\text{H}^-$  acceptors on the value of Gibbs free energy change ( $\Delta\text{G}$ ), the relative Gibbs free energy change ( $\Delta\Delta\text{G}$ ) was calculated in this work by calibrating to the B–H cleavage at B(12) position in  $[\text{CB}_{11}\text{H}_{12}]^-$ . Figure 3a presents the  $\Delta\Delta\text{G}$ , indicating that the B(12) position is the most favorable for  $\text{H}^-$  loss, followed by B(7) and, ultimately, B(2). On the contrary, the  $\Delta\Delta\text{G}$  trend of losing  $\text{H}^+$  is exactly opposite that the proton at B(2) was most activated. Given that the regioselectivity was favored at B(12) site, it was more likely to undergo a hydride abstraction pathway. Simultaneously, we calculated the  $\Delta\Delta\text{G}$  for various B–H bonds in  $[\text{CB}_{11}\text{H}_{12}]^-$  analogues, including  $[\text{B}_{12}\text{H}_{12}]^{2-}$  and  $m\text{-C}_2\text{B}_{10}\text{H}_{12}$ . By comparison, it is easier to lose  $\text{H}^-$  in  $[\text{B}_{12}\text{H}_{12}]^{2-}$ , which lacks a carbon vertex, as the  $\Delta\Delta\text{G}$  is  $-12.2$  kcal/mol. However, *meta*-carborane 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$  is more difficult to lose  $\text{H}^-$  with  $\Delta\Delta\text{G}$  of B–H in any position exceeding 20 kcal/mol. To check this calculation results, we carried out the experimental works, and found neither *ortho*- $\text{C}_2\text{B}_{10}$ , *meta*- $\text{C}_2\text{B}_{10}$ , nor *para*- $\text{C}_2\text{B}_{10}$  reacted with  $[\text{AcNH-TEMPO}]^+ [\text{BF}_4]^-$ , and the single-substituted product could not be obtained in  $[\text{B}_{12}\text{H}_{12}]^{2-}$ . These reinforced the reaction process involved the loss of  $\text{H}^-$  rather than the loss of  $\text{H}^+$ .

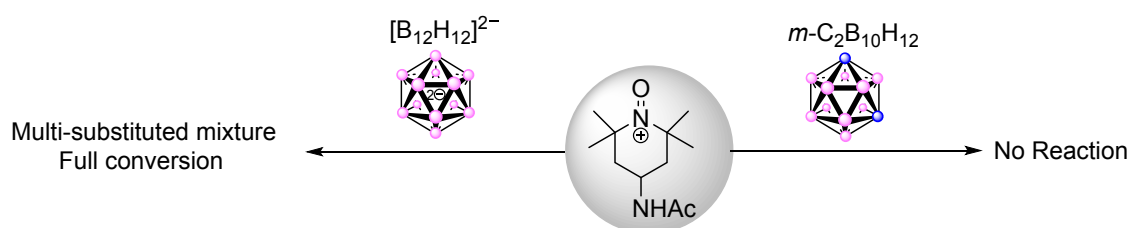
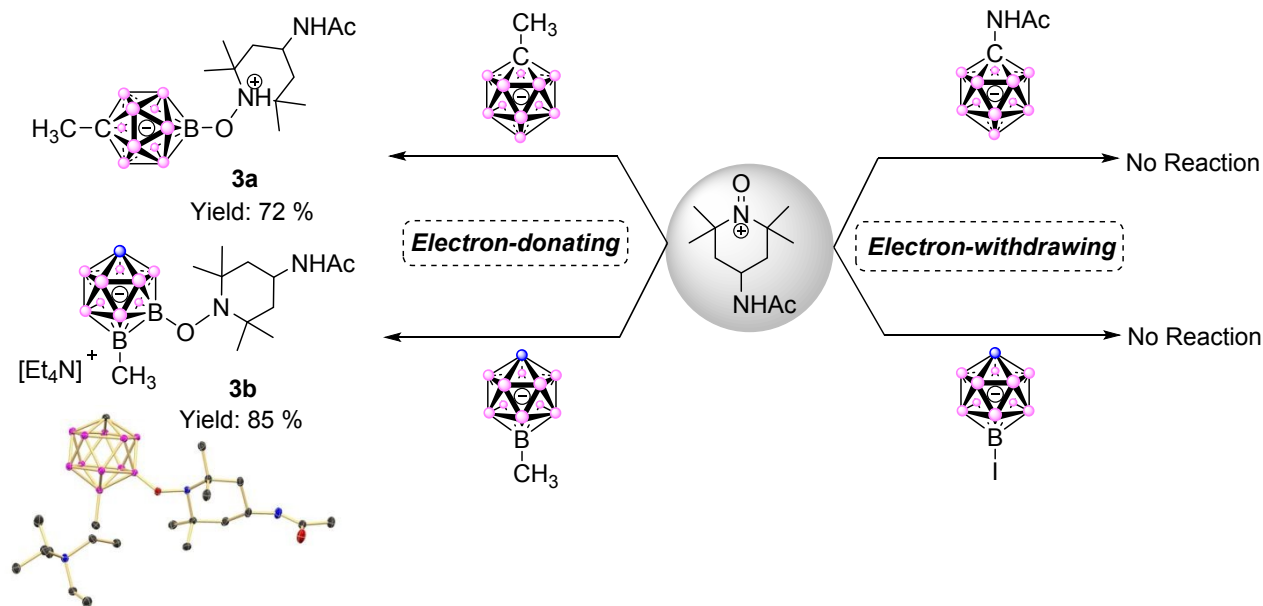
Further evidence came from the fact that the compound did not react with  $[\text{AcNH-TEMPO}]^+ [\text{BF}_4]^-$  when the electron-withdrawing iodine substituent occupied position B(12). In contrast, the coupling product at position 7 (the second most likely position to lose  $\text{H}^-$ ) was obtained with an isolated yield of 85% when the electron-donating effect [ $12\text{-CH}_3\text{-CB}_{11}\text{H}_{11}]^-$  was used. Additionally, theoretical calculations indicated that the  $\Delta\Delta\text{G}$  for  $\text{H}^-$  loss at this position was reduced by 0.9 kcal/mol compared to  $[\text{CB}_{11}\text{H}_{12}]^-$ , which further supported that the reaction involved a hydride anion abstracting ( $\text{H}^-$  loss) process. In addition, when electron-donating  $-\text{CH}_3$  and electron-withdrawing  $-\text{NHAc}$  substituents were attached to the C vertex of  $[\text{CB}_{11}\text{H}_{12}]^-$ , the results were consistent with our expectations: desired product was obtained with an isolated yield of 72% when [ $1\text{-CH}_3\text{-CB}_{11}\text{H}_{11}]^-$  was used, whereas [ $1\text{-AcNH-CB}_{11}\text{H}_{11}]^-$  did not undergo conversion (Fig. 3c).



## a) DFT Calculations



## b) Reactivity of different boron clusters

c) Reactivity of different substituents of [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>

**Fig. 3** (a) Relative Gibbs free energy change ( $\Delta\Delta G$ ) for the heterolytic cleavage of B–H bonds, showing the loss of H<sup>-</sup> (red) and H<sup>+</sup> (blue); (b) Reactivity of different boron clusters and (c) Reactivity of different substituents of [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> anion.

Subsequently, the transition state for B(12)–H heterolysis was investigated (Figure 4a-c). Initially, we tried to find a 4-member ring type transition state to mediate concerted H-abstraction and B–O bond formation, but failed due to the large steric hindrance between oxoammonium cation and the [CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> cage. However, a reasonable transition state was

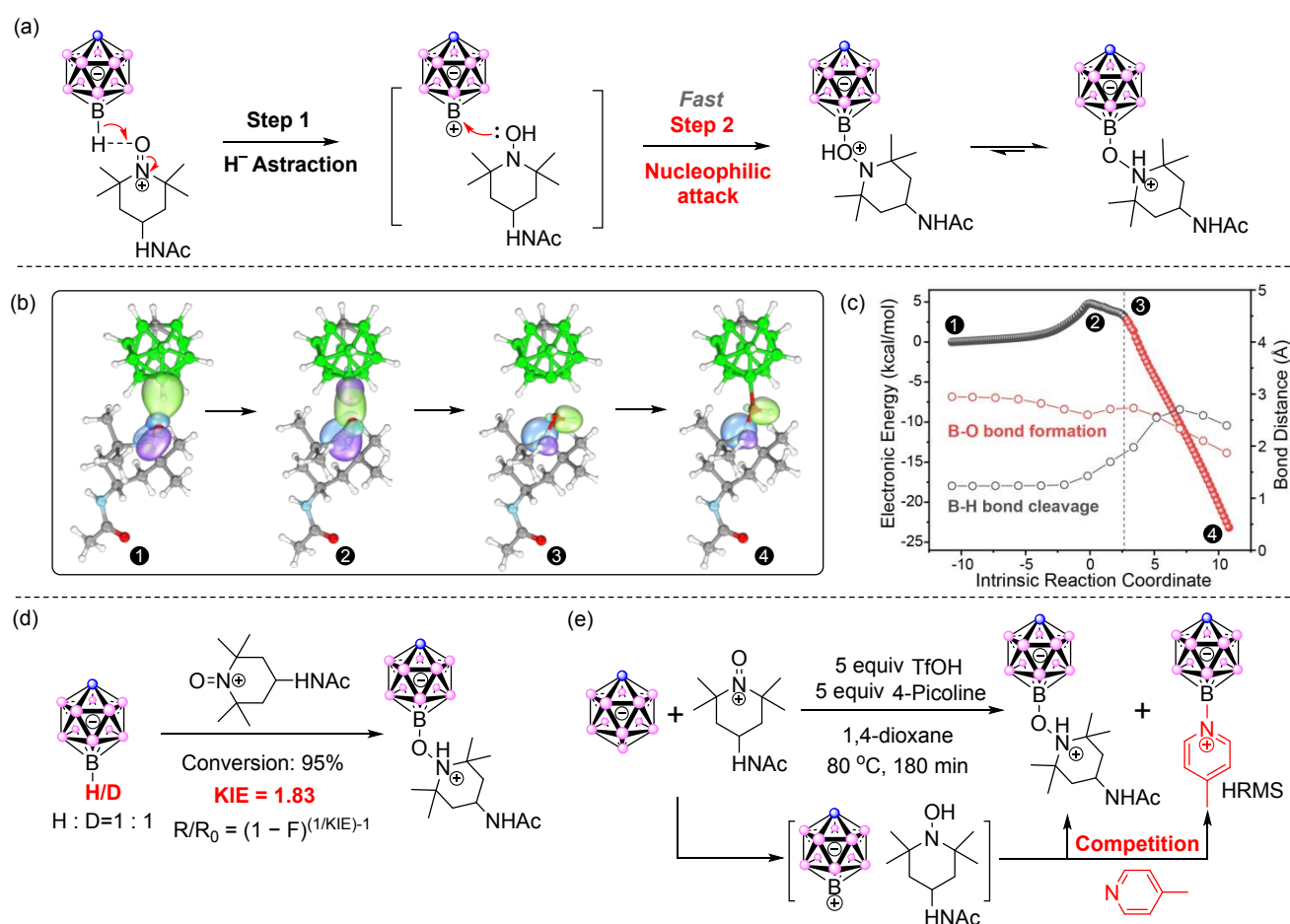
found for the transfer of H<sup>-</sup> to O atom at oxoammonium cation, and the intrinsic reaction coordinate (IRC) analysis suggested the subsequent O–B bond formation after the formation of the [CB<sub>11</sub>H<sub>11</sub>][hydroxylamine] pair. The corresponding activation Gibbs free energy ( $\Delta G^\ddagger$ ) was 21.1 kcal/mol, owing 4.2 kcal/mol favored to the unreactive *meta*-B–H bonds ( $\Delta G^\ddagger = 25.3$



kcal/mol). The intrinsic bond orbitals (IBOs) along the reaction coordinate supposed the hydride anion abstraction by oxoammonium cation. As illustrated in Figure 4b, apparent electron flow was observed from the  $[CB_{11}H_{12}]^-$   $\sigma$  orbital to the  $NO \pi$  orbital and formed transient intermediate  $CB_{11}H_{11}$  and hydroxylamine, indicating the apparent hydride anion transfer. Besides, the IRC plot indicated that this reaction proceeded in two steps and had a high-energy transition state (Figure 4c). In the first step, the H atom of  $[CB_{11}H_{12}]^-$  moves toward to the oxoammonium salts, resulting in B–H bond cleavage and O–H bond formation (blank balls). The B–O distance decreases from 2.95 to 2.60 Å. In the next step, starting from the red balls, hydroxylamine attacks the electrophilic intermediate, forming the final product. The B–O distance further decreases from 2.60 to 1.87 Å. The formation of the B–O–N coupling product was exergonic by 56.3 kcal/mol. Based on the above calculations, we proposed the following mechanism: firstly, the  $[CB_{11}H_{12}]^-$  is oxidized by  $[AcNH-TEMPO]^+[BF_4]^-$  to form the paired

intermediate,  $[CB_{11}H_{11}][hydroxylamine]$ . Subsequently, hydroxylamine, acting as a nucleophilic reagent, attacked the intermediate  $CB_{11}H_{11}$  to form the B–O–N compound as the final product.

To support the proposed mechanism involving hydride abstraction and subsequently nucleophilic substitution, hydrogen kinetic isotope effect (KIE) experiments were conducted (Figure 4d).  $[H-CB_{11}D_{11}]^-$  was synthesized from  $[CB_{11}H_{12}]^-$  via microwave reaction in  $D_2O$  containing 20 wt% DCl. A 1:1 reaction between  $[CB_{11}H_{12}]^-$  and  $[H-CB_{11}D_{11}]^-$  was conducted under standard reaction conditions. At 95% conversion, an apparent KIE of 1.83 was calculated by the equation  $R/R_0 = (1 - F)^{(1/KIE)-1}$  (Figure 4d).<sup>49</sup> In general, primary KIEs typically range from 2 to 8, while secondary KIEs fall within 1.0 to 1.2.<sup>50</sup> The observed KIE value of 1.83 is closer to the range of primary KIEs, suggesting that the cleavage of the B–H/D bond was the rate-determining step.



**Fig. 4** (a) Proposed mechanism; (b) The intrinsic bond orbitals (IBOs) illustrate the electron flow during the reaction between  $[CB_{11}H_{12}]^-$  and oxoammonium cation and proposed mechanism; (c) The change of electronic energies along the intrinsic reaction coordinate for the sequentially occurred step 1 (blank balls) and step 2 (red balls). The dot lines illustrated change of B–H (black) and B–O (red) bond distances along the intrinsic reaction coordinate; (d) Determination of KIE for H–H; (e) Capture experiments.

In addition, the radical pathway was excluded by the control experiment and electron paramagnetic resonance spectroscopy (EPR). The reaction could run as the same when in the dark. The  $[AcNH-TEMPO]$  radical could not take the place of  $[AcNH-TEMPO]^+[BF_4]^-$  to oxidize  $[CB_{11}H_{12}]^-$  under standard conditions.

No significant signals were detected during the reaction by EPR (Figure S2).

Next, in order to prove the nucleophilic step, 4-methylpyridine, a nucleophile, was put into the reaction and found to be attached to  $[CB_{11}H_{12}]^-$  anion in the presence of



trifluoromethanesulfonic acid (Figure S3), which supported a  $S_N1$  mechanism. Besides, the oxide form of 4-methylpyridine-N-oxide did not appear, excluding the 4-methylpyridine oxidation route. Furthermore, when 4-methylpyridine was replaced with 4-methoxypyridine, the product with 4-methoxypyridine attached to  $[CB_{11}H_{12}]^-$  anion was also observed in HRMS (Figure S4). Water, acting as a nucleophile, was also employed in varying amounts to perform the capturing reaction. Anhydrous 1,4-dioxane, untreated commercial 1,4-dioxane, and 1,4-dioxane containing 10 v% water were used as solvents. HRMS data revealed an increasing ratio of hydroxyl-substituted  $[CB_{11}H_{12}]^-$  anion to the hydroxylamine-substituted  $[CB_{11}H_{12}]^-$  anion (Figure S5-7). However, the yields of these captured compounds were relatively low, making isolation and precise determination of the ratio challenging. This could be attributed to the preferential reaction within the in-situ-formed  $[CB_{11}H_{11}]$  [hydroxylamine] pair, which suppresses competition from other nucleophiles. In brief, these experimental results demonstrated that the reaction proceeded in two steps, likely following an  $S_N1$ -type nucleophilic substitution mechanism rather than an  $S_N2$ . The oxidation of the B-H bond in  $[CB_{11}H_{12}]^-$  by oxoammonium salts leads to hydride abstraction, which then facilitates nucleophilic attack by hydroxylamine. This results in the highly selective formation of B(12) oxygen derivatives of the  $[CB_{11}H_{12}]^-$  anion. Based on these observations, we propose a novel mechanism: oxoammonium oxidation-induced nucleophilic substitution (OINS).



Entry	Radical	Structure	Yield
1			4a 96 %
2			4b 78 %
3			4c 88 %
4			4d 55 %
5			4e 92 %

Fig. 5 Substrate scope of B(12) derivatives.

Finally, we employed various N-O compounds for the reaction to verify the universality of the method. All reactions were conveniently set up and conducted under ambient air conditions. Considering that oxoammonium cations can be generated by the disproportionation of nitroxide radicals in acidic media, we attempted to conduct a one-pot reaction by directly employing nitroxide radicals. As shown in Figure 5, common piperidine nitroxide radicals also worked. Additionally, for some substrates with active groups, moderate to high yields were achieved. Moreover, during the reaction with free radicals, we detected the structure of the hydroxy-oxoammonium adduct, which further proved that the mechanism of the reaction involving free radicals first generating hydroxy-oxoammonium adducts and oxoammonium cations via disproportionation. This method enables the construction of similar B-O-N structures with various nitroxide radicals, providing a reference for potential future applications.

## Conclusions

In conclusion, we have developed a new strategy to achieved high selectivity B-H functionalization of  $[CB_{11}H_{12}]^-$ , and OINS mechanism was proposed. With this approach, a series of novel and stable B-O-N derivatives were synthesized.  $S_N1$  type nucleophilic substitution reactions on aromatic rings have long been recognized as challenging.<sup>51-53</sup> Our research indicates that the successful nucleophilic substitution on the  $[CB_{11}H_{12}]^-$  anion is attributed to three primary factors: 1) the B-H bond is more easily cleaved compared to the C-H bond in conventional aromatic systems; 2) Oxoammonium cations can abstract the hydride ( $H^-$ ) due to their unique oxidizing abilities; and 3) the resulting product is a zwitterionic compound, which contributes to its stability. This work establishes a novel regioselective derivatization method and advances the mechanistic understanding of derivatization in aromatic compounds.

## Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the ESI.† And all data can be obtained from the authors.

## Author contributions

H.L. conceived the project and supervised the work with Y.W. and J.Y.. W.S. conducted the experiments and drafted the original manuscript. Y.J. contributed to the development of the methodology. Y.W. performed theoretical calculations. Z.W. participated in the experimental design. J.S. provided critical feedback and assisted in data analysis. S.D. offered constructive comments. All authors discussed the results, reviewed, and contributed to the final manuscript.

## Conflicts of interest



There are no conflicts to declare.

## Acknowledgements

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## Data Availability Statement

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The data supporting this article have been included as part of the Supplementary Information. And all data can be obtained from the authors. Crystallographic data for compounds **2**, **3b**, **4b** and **4c** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under accession numbers 2407119–247122. The 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).

