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Recent Trends in Triarylborane Chemistry: Diversification of Structures and Reactivity via *meta*-Substitution of the Aryl Groups

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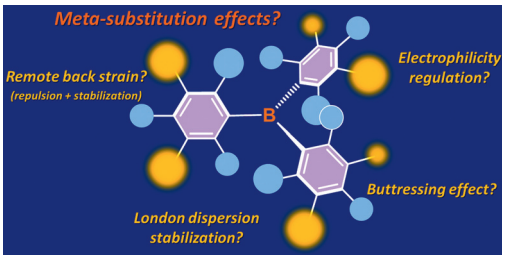

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Abstract This Short Review summarizes the synthesis and applications of triarylboranes (BAr_3), including both homoleptic and heteroleptic species, with a focus on the modification of their electronic and structural properties via the introduction of *meta*-substituents with respect to the B atoms to their Ar groups. This approach constitutes a complementary alternative to conventional strategies for the design of BAr_3, which are usually based on a modification of their *ortho*- and/or *para*-substituents. An initial analysis revealed that CH_3 and F are the most common *meta*-substituents in hitherto reported BAr_3 (apart from the H atom). Thus, an extensive exploration of other substituents, e.g., heavier halogens, longer or functionalized alkyl groups, and aryl groups, will increase our knowledge of the structure and reactivity of BAr_3 and eventually lead to a range of new applications.

Key words boranes, Lewis acids, catalysis, main group elements

Yoichi Hoshimoto received his M.Sc. and Ph.D. from Osaka University in 2013. He then joined the Frontier Research Base for Global Young Researchers, Osaka University as a tenure-track assistant professor (2013–2018). Subsequently, he was promoted to associate professor in the Department of Applied Chemistry, Faculty of Engineering, Osaka University (2018). Since 2023, he has been recognized as an Outstanding Young Researcher in the Center for Future Innovation (CFi), Faculty of Engineering, Osaka University. He is one of the Thieme Chemistry Journals Awardees 2024.

1 Introduction

Triarylboranes (BAr_3), including both homoleptic and heteroleptic species, are typical Lewis acids that are widely used as catalysts, activators, sensors, and bio-imaging agents.[1] In the field of main group catalysis in particular, recent progress in the field of frustrated Lewis pairs (FLPs)[2] has led to a significant structural diversification of halogenated triarylboranes beyond the archetypical $B(C_6F_5)_3$. This structural diversification can be achieved by the introduction of substituents to the Ar groups at the *ortho*-, *meta*-, and/or *para*-positions, with respect to the boron center, as part of a strategy to control the Lewis acidity of BAr_3.[3,4] These strategies to control the Lewis acidity focus on regulating the accessibility (a kinetic aspect) and energy (a thermodynamic aspect) of the empty p orbital at the boron center.

Strategies that substitute *meta*-F and/or *para*-F atoms in $B(C_6F_5)_3$ with more or less electron-withdrawing substituents have been applied to prepare more or less electrophilic BAr_3 derivatives through regulation of the electron affinity at the boron center.[1a,b,3,5] Strategies that regulate the steric repulsion between a Lewis base (LB) counterpart (front strain; Figure 1, left) through modulation of the size of the *ortho*-substituents have also been widely explored.[6] Alter-

natively, the Lewis acidity of BAr_3 can be modulated by regulating the intramolecular repulsion between the Ar groups of tetrahedral LB–borane adducts (back strain; Figure 1, right). In this context, the classical concept of back strain refers to the repulsion between *ortho*-substituents.[7] Moreover, Hoshimoto and co-workers recently discussed the concept of 'remote' back strain based on the repulsion and supportive non-covalent interactions (NCIs) between *meta*-substituents themselves and/or between *meta*-substituents and substituents in the LBs.[8–10] During our efforts to develop an effective method to finely tune the (catalytic) reactivity of BAr_3, we discovered that only a limited number of substituents had been introduced at the *meta*-positions for the derivatization of BAr_3.

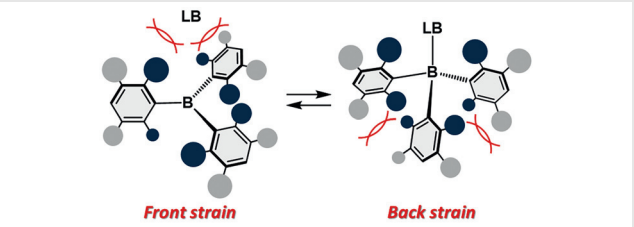


Figure 1 A schematic illustration of front strain and (remote) back strain generated between BAr_3 and Lewis bases (LBs).

Hence, a review that summarizes the structure and use of *meta*-substituted BAr_3 will be a worthwhile addition to previously reported reviews that have predominantly focused on the derivatization of BAr_3 via substitution at the *ortho*- and *para*-positions.[1a,b] Moreover, we previously confirmed that over 80% of *ortho*- and *meta*-substituents in BAr_3, along with 50% of *para*-substituents, consist of H, F, and CH_3 groups, based on our analysis of the 98 homoleptic BAr_3 compounds synthesized up to and including 2020 (as found using SciFinder in February 2024) (Figure 2). In particular, F or CH_3 *ortho*-disubstituted compounds were found to have been frequently explored for the kinetic protection of the vacant p orbital on boron by regulation of the front strain. Conversely, the impact of *meta*-disubstitution on the Lewis acidity of BAr_3 compounds has been less well studied, probably due to the limited number of synthetic routes to *meta*-F_2- or *meta*-$(CH_3)_2$-substituted species.[9,11] This Short Review thus aims to summarize the structures and applications of *meta*-substituted homoleptic and heteroleptic BAr_3 species and to shed light on the importance of such structural modifications in the context of regulating the reactivity of BAr_3 compounds.

2 Scope of this Review

This Short Review analyzes both homoleptic and heteroleptic BAr_3 compounds whose synthesis had been reported up until February 2024. BAr_3 species that have merely been explored theoretically are not included. In addition, boranes that have *meta*-H, -F, and -CH_3 substituents are beyond the scope of this Short Review , even though the corresponding homoleptic species were considered when Figure 2 was prepared, to avoid significant overlap with previous reports.[1a,b] Furthermore, several BAr_3 compounds with 2,6-dimethylaryl groups (e.g., mesityl groups) and *ortho*-bridged planar structures have also been omitted, given that these compounds have already been summarized in other critical reviews.[1c,12–14]

2.1 The Electronic and Steric Influence of *meta*-Substituents

A fundamental and highly effective approach to modulate the Lewis acidity of BAr_3 is to regulate the energy levels of the unoccupied p orbital on the boron atom, i.e., modulating the intrinsic electrophilicity. Unsurprisingly, chemists have explored the introduction of (strongly) electron-donating or -withdrawing substituents at the *meta*- and/or *para*-positions of the Ar groups. The introduction of the strongly electron-withdrawing CF_3 group in 3,5-$(CF_3)_2C_6H_3$ (Ar^F) has stimulated the curiosity of many chemists.[15–20] In 2012, Ashley and co-workers demonstrated the synthesis of BAr^F_3 (**B[1]**) on a practical scale via a reaction between a

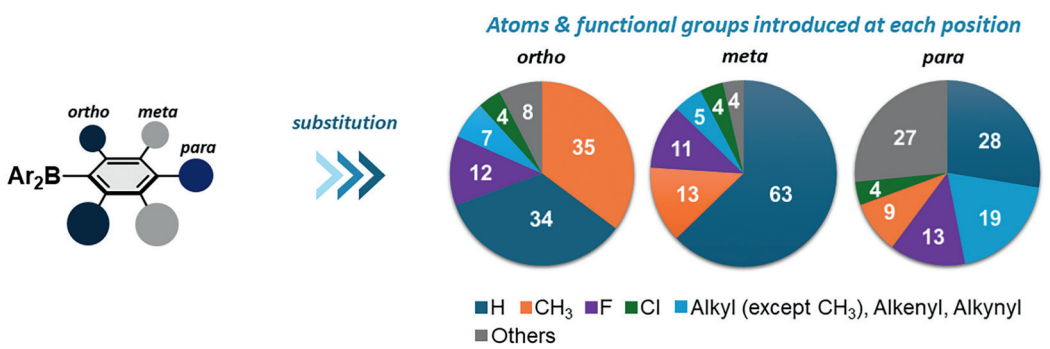
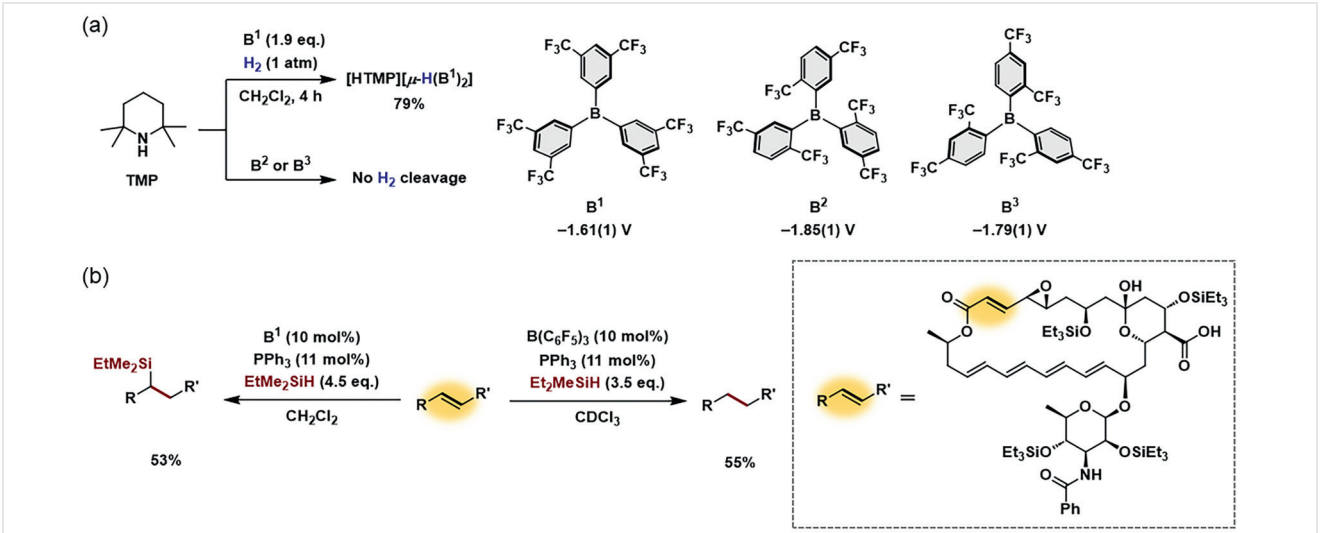


Figure 2 Analysis of the substituents introduced at the *ortho*-, *meta*-, and *para*-positions in 98 homoleptic BAr_3 species (as found using SciFinder in February 2024); the relative ratio of each substituent type is given, e.g., for a BAr_3 including a 2,4,6-trimethyl group, two *ortho*- and one *para*-CH_3 groups are counted.



Scheme 1 (a) Heterolytic cleavage of H_2 via the combination of TMP and **B¹**–**B³**, with their formal reduction potentials (*vs.* $[FeCp_2]^{0/+}$ [V]) and (b) the reduction of a bioactive compound using **B¹** or $B(C_6F_5)_3$.

Grignard reagent including the Ar^F ligand and $BF_3{\cdot}OEt_2$.[15a] As expected, the Lewis acidity of **B¹** was confirmed experimentally, using the Gutmann–Beckett method and $Et_3P{=}O$ as a probe for a ^{31}P NMR analysis, to be higher than that of $B(C_6F_5)_3$. Conversely, when *trans*-crotonaldehyde was employed as a probe for the ^1H NMR analysis (Child's method), **B¹** was found to exhibit lower Lewis acidity than $B(C_6F_5)_3$. Ashley and co-workers also explored the reactivity of an FLP comprised of **B¹** and 2,2,6,6-tetramethylpiperidine (TMP) with H_2, which afforded the salt $[HTMP][\mu\text{-}H(\mathbf{B^1})_2]$ (Scheme 1a).[15a] In contrast, Blagg, Lawrence, and Wildgoose reported that the heterolytic cleavage of H_2 did not occur when FLPs of TMP and $B(2,5\text{-}(CF_3)_2C_6H_3)_3$ (**B²**) or $B(2,4\text{-}(CF_3)_2C_6H_3)_3$ (**B³**) were employed.[17a] The authors also rationalized the increased electrophilicity of **B¹** relative to **B²** or **B³** based on the analysis of the formal reduction potentials of all three compounds. Using **B¹** in another catalytic system, Gagné and co-workers showed that different products were obtained when a specific combination of **B¹**/$EtMe_2SiH$ or $B(C_6F_5)_3/Et_2MeSiH$ was used in the catalytic reduction of natamycin (Scheme 1b).[18a–d]

Pápai, Soós, and co-workers also investigated the electronic effects of *meta*-substituents through a comparison of the Lewis acidity of a series of heteroleptic BAr_3 compounds (**B⁴**–**B¹⁵**) based on their hydride ion affinity (HIA) and the Gutmann–Beckett method (Figure 3).[11] These authors showed that the replacement of the *meta*-H atom with an F atom significantly enhances the Lewis acidity, whereas a replacement of a *meta*-Cl atom in either the Mes or 2,6-Cl_2-aryl moieties results in negligible changes.

The steric effects imparted by *meta*-substituents have been examined from three main perspectives: (1) the buttressing effect; (2) London dispersion forces; and (3) remote back strain as a sum of the electronic/steric repulsion

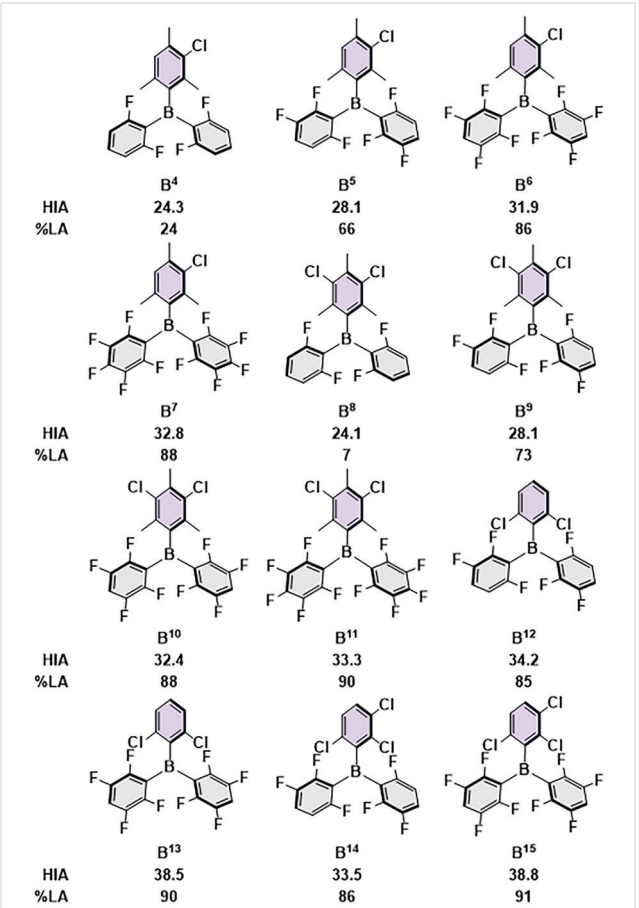
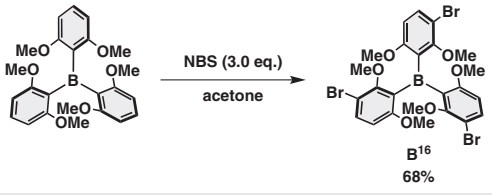


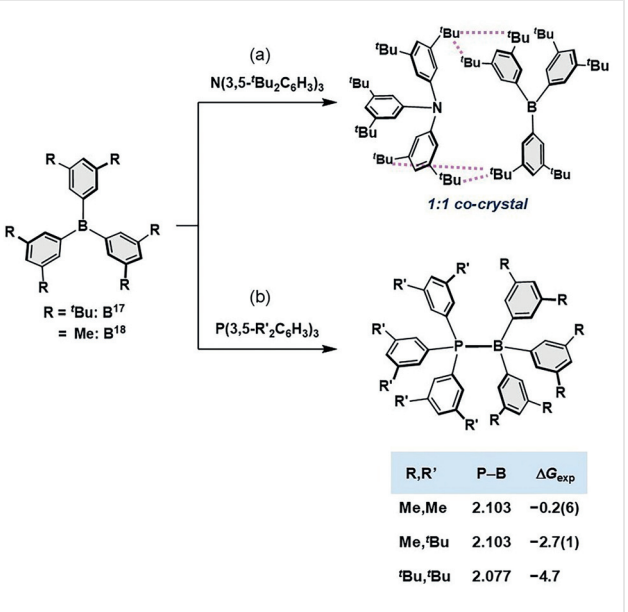
Figure 3 Comparison of the theoretical HIA (kcal mol^{-1}) and relative Lewis acidity (%LA) of **B⁴**–**B¹⁵**; %LA values were determined using the Gutmann–Beckett method with $Et_3P{=}O$ and are calculated with respect to $B(C_6F_5)_3$ (%LA = 100).



Scheme 2 Synthesis of **B[16]**.

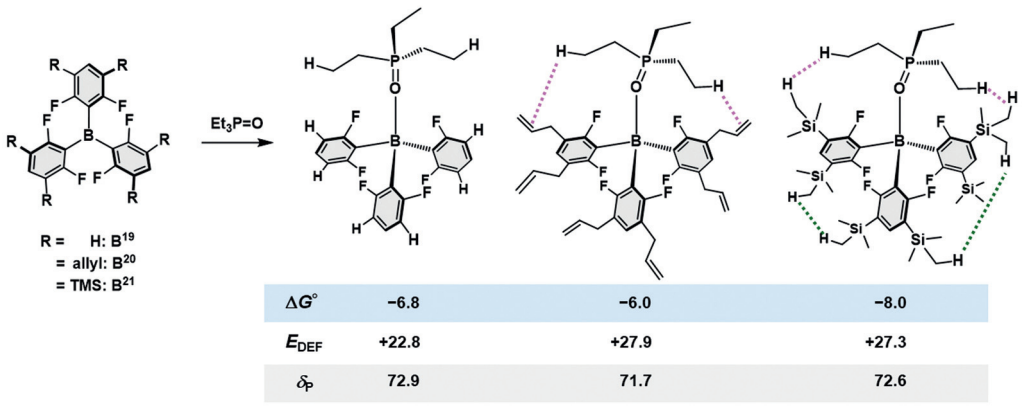
and NCIs. For example, Wada and co-workers synthesized B(3-Br-2,6-$(MeO)_2C_6H_2)_3$ (**B[16]**) through the direct bromination of air-stable B(2,6-$(MeO)_2C_6H_2)_3$ with *N*-bromosuccinimide (NBS) (Scheme 2).[21] While B(2,6-$(MeO)_2C_6H_2)_3$ forms isolable adducts with primary amines and ammonia, **B[16]** does not form such adducts with the same amines. The authors attributed this reactivity difference to the buttressing effect caused by the *meta*-Br atoms, i.e., the Br atoms push the adjacent MeO groups closer to the boron atom thus hindering access of the amines to the boron center. The electron-withdrawing nature of the Br atoms was not considered in this case.

Slootweg and co-workers recently proposed that London dispersion forces play a critical role in stabilizing encounter complexes formed between BAr_3 and LBs (Scheme 3a).[22a] The authors observed the formation of 1:1 co-crystals comprised of B(3,5-^{t}Bu$_2$C$_6$H$_3$)$_3$ (**B[17]**) and N(3,5-^{t}Bu$_2$C$_6$H$_3$)$_3$. Based on theoretical calculations, the authors concluded that interaction energies between the *meta*-^{t}Bu groups in **B[17]** and those in N(3,5-^{t}Bu$_2$C$_6$H$_3$)$_3$ are significantly larger than the corresponding energies formed between **B[1]** and N(3,5-^{t}Bu$_2$C$_6$H$_3$)$_3$. Hansen, Paradies, and co-workers further studied the importance of dispersion forces based on a combined experimental and theoretical approach.[22b] These authors expanded the discussion to include the B(3,5-$R_2C_6H_3)_3$ (R = ^{t}Bu, **B[17]**; Me, **B[18]**) and P(3,5-$R'_2C_6H_3)_3$ (R' = ^{t}Bu, ^{i}Pr, Me) pairs and concluded that the Lewis acid/base adducts generally become more stable as the size of the dispersion-energy donor increases, albeit that their stability is sensitive to the solvation conditions (Scheme 3b). In this study, the reactivity of B(3,5-^{i}Pr$_2$C$_6$H$_3$)$_3$ was not explored due to difficulties associated with synthesis and stability.



Scheme 3 London dispersion energies stabilize (a) the amine-borane encounter complex involving **B[17]**, and (b) the phosphine-borane adducts involving **B[17]** and **B[18]**; the reported P–B bond lengths (Å) and association energies of the Lewis pairs (ΔG_{exp} in kcal mol^{-1}) are shown.

From a different perspective, Hoshimoto and co-workers also explored how the physical and electronic properties of *meta*-substituents increase/decrease the stability of borane-LB adducts, and hence, prevent/promote the dissociation of LBs from the adducts to generate free BAr_3 (or FLP species) (Scheme 4).[8–10] The authors focused on the concept of 'remote' back strain (Figure 1b), which is defined as the sum of repulsive (steric/electronic) and attractive (NCIs) in-



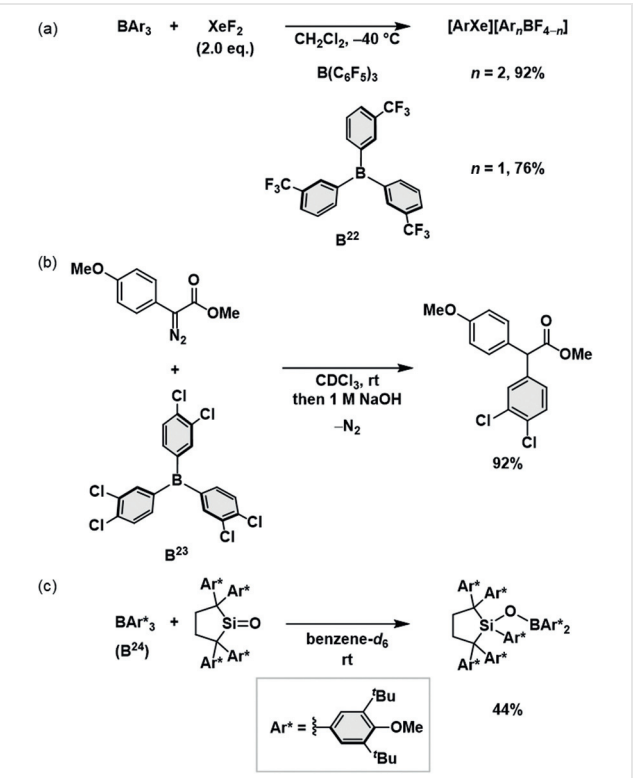
Scheme 4 Comparison of theoretical parameters for the formation of Et_3P=O–**B[n]** (*n* = 19–21) adducts, i.e. relative Gibbs energies ($\Delta G°$ in kcal mol^{-1} with respect to [**B[n]** + Et_3P=O]), and deformation energies (E_{DEF} in kcal mol^{-1}). The chemical shifts in ^{31}P NMR, δ_P, obtained in the reaction between **B[19]**–**B[21]** and Et_3P=O (0.3 eq.) in CH_2Cl_2 are also given.

teractions that occur between the *meta*-substituents of the tetrahedral BAr_3 units in the borane-LB adducts (or a transition state of the borane deformation). In general, these *meta*-substituents must be effectively separated in the free trigonal planar BAr_3 structure.[9] To quantify the remote back strain, homoleptic boranes bearing 2,6-F_2-3,5-allyl$_2C_6H_3$ (**B^{20}**) and 2,6-F_2-3,5-$TMS_2C_6H_3$ (**B^{21}**) were synthesized for a comparison with B(2,6-$F_2C_6H_3)_3$ (**B^{19}**), as these boranes exhibit nearly identical intrinsic Lewis acidity (the LUMO energy levels) and front strain toward LBs. The relative Gibbs energy values ($\Delta G°$) for the formation of an adduct with a LB (the LBs used in the corresponding work were Et_3P=O, H_2O, CO, THF, and NMe_3) and the deformation energy (E_{DEF}),[3a] which is an energetic penalty paid for the geometrical change at the boron center upon adduct formation, were evaluated for each of these three boranes. For example, when Et_3P=O was used as the LB, the E_{DEF} values increased in the order **B^{19}** < **B^{21}** < **B^{20}**, which is consistent with the trend determined via the Gutmann–Beckett method. However, the $\Delta G°$ values showed a different trend and increased in the order **B^{21}** < **B^{19}** < **B^{20}**. This discrepancy was rationalized by considering the multiple NCIs formed between the *meta*-TMS groups themselves and the *meta*-TMS and *P*-Et groups in the Et_3P=O–**B^{21}** adducts. Finally, the authors concluded that repulsion and the NCIs generated between *meta*-substituents are essential for estimating and regulating the remote back strain for fine-tuning the catalytic activity of BAr_3. It should also be noted that **B^{20}** is a rare example of a liquid BAr_3.

In another report, *meta*-substituents were used as a tool for monitoring the stereoisomerization of BAr_3. Mislow and co-workers demonstrated that the stereoisomerization in B(3-^{i}Pr-2,4,6-Me_3C_6H)(2,6-$Me_2C_6H_3)_2$ proceeds via a two-ring flip mechanism, as confirmed by temperature-dependent ^{1}H NMR spectroscopy based on the diastereotopic nature of the *meta*-^{i}Pr group.[23]

2.2 Molecular Transformations Mediated by *meta*-Substituted Boranes

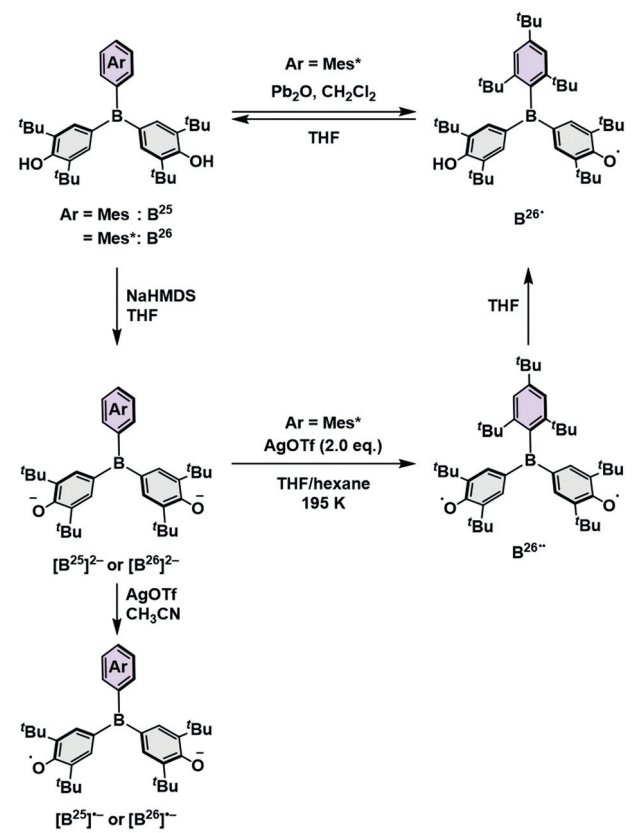
Some *meta*-substituted BAr_3 compounds have been applied as aryl-transfer reagents. Frohn and co-workers studied the migration of an aryl group from an electrophilic BAr_3 species, such as B($C_6F_5)_3$ and B(3-$CF_3C_6H_4)_3$ (**B^{22}**), to XeF_2 in CH_2Cl_2, eventually affording [ArXe][$ArBF_3$] (Ar = C_6F_5 or 3-$CF_3C_6H_4$) (Scheme 5a).[24] In 2019, Melen, Wirth, and co-workers developed an aryl-transfer reaction from BAr_3 to various α-aryl-α-diazoacetates (Scheme 5b).[25] They found that the number of aryl groups that are transferred depends on the Lewis acidity of BAr_3, e.g., B($C_6F_5)_3$ and B(3,4,5-$F_3C_6H_2)_3$ can transfer all three Ar groups, whereas B(3,4-$Cl_2C_6H_3)_3$ (**B^{23}**) can only transfer one of its three 3,4-$Cl_2C_6H_3$ groups. Ishida, Iwamoto, and co-workers also reported on the migration of aryl groups from BAr_3, including B($C_6F_5)_3$, **B^1**, and BAr^*_3 (Ar* = 3,5-^{t}Bu$_2$-4-$MeOC_6H_2$; **B^{24}**), to a dialkylsilanone, which was proposed to proceed via the formation of a Si=O–B adduct (Scheme 5c).[26] This report nicely demonstrates that BAr_3 can enhance the reactivity of an unsaturated silicon center upon adduct formation, which is often seen in the activation of carbonyl compounds by Lewis acids.



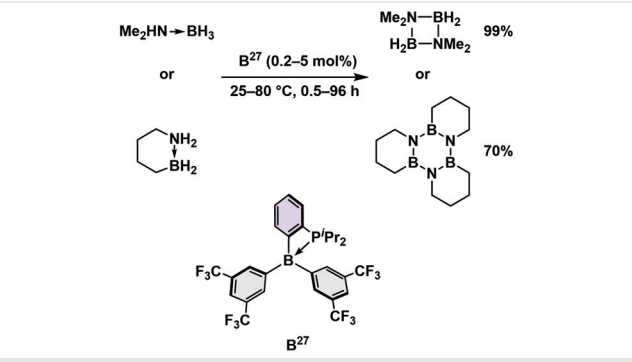
Scheme 5 Aryl-transfer reactions from BAr_3 to (a) XeF_2, (b) a diazo ester, and (c) a dialkylsilanone.

Chiu and co-workers reported heteroleptic BAr_3 species **B^{25}** and **B^{26}**, which bear *para*-OH groups (Scheme 6).[27] Trivalent boron compounds such as these contain Lewis basic and Brønsted acidic functional groups and it is not always facile for these moieties to co-exist within the same compound. Interestingly, ^{t}Bu groups were introduced at the *meta*-positions of bulky 1,3,5-$R_3C_6H_2$ (**B^{25}**: R = Me (Mes); **B^{26}**: R = ^{t}Bu (Mes*)) group at the boron center. Moreover, these authors explored the oxidation of these boranes and confirmed that boryl analogues of the galvinoxy radical, such as [**B^{25}**]$^{\bullet-}$ and [**B^{26}**]$^{\bullet-}$, were generated. The introduction of boron decreases the quinoidal character of the phenoxyl radical and activates the open-shell species.

Bourissou and co-workers reported the preparation of the *ortho*-phenylene bridged phosphine-borane compound **B^{27}**, which contains two Ar^F groups at the boron center (Scheme 7).[28] Based on NMR, single-crystal X-ray diffraction, and DFT analyses, an intramolecular coordination interaction between the phosphorus and the boron centers



Scheme 6 Oxidation of **B[25]** and **B[26]** (Mes* = 1,3,5-^{t}Bu$_3$C$_6$H$_2$).

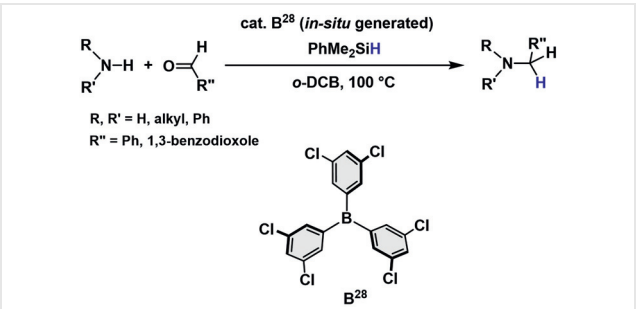


Scheme 7 Dehydrogenation of cyclic amine-boranes catalyzed by **B[27]**.

was proposed. The catalytic reactivity of **B[27]** was evaluated in the dehydrogenation of acyclic and cyclic (di)amine-boranes.

One of the most extensively explored fields in main group catalysis is the reduction of unsaturated compounds with BAr_3 catalysts.[2,29] Needless to say, *meta*-substituted BAr_3 have also contributed to the significant development of this important field. For example, Pápai, Soós, and co-workers reported the catalytic hydrogenation of aldehydes, ketones, and enones using H_2 and **B[12]**–**B[15]**.[30]

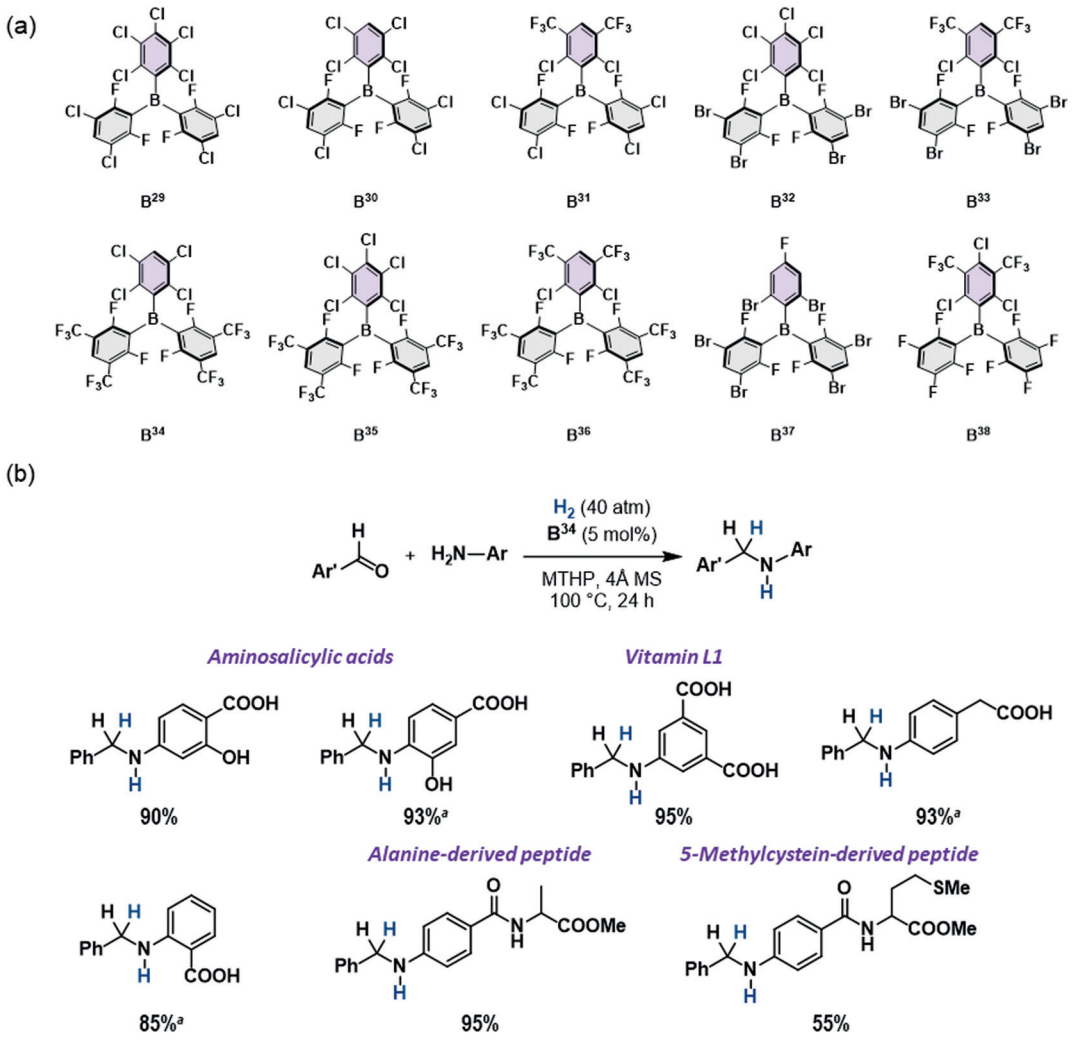
The use of hydrosilanes as a reductant is another practical example of the main-group-catalyzed reduction of unsaturated compounds. For example, Ingleson and co-workers pioneered the development of a main-group-catalyzed reductive alkylation of amines with carbonyl compounds and hydrosilanes in the presence of $B(C_6F_5)_3$, BPh_3, or $B(3,5\text{-}Cl_2C_6H_3)_3$ (**B[28]**).[31] In particular, the *in situ* generation of **B[28]** from $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$ enabled the transformation of primary amines whose conjugate acids span pK_a values of 10.6 to 18.5 in MeCN (Scheme 8).[31a]



Scheme 8 Reductive alkylation of amines catalyzed by **B[28]**, generated from $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$ *in situ*.

Between 2017 and 2018, Hoshimoto and co-workers and Soós and co-workers independently reported the BAr_3-catalyzed reductive alkylation of amines with aldehydes and H_2, where H_2O is generated as the sole byproduct.[7,32] In the former case, a catalyst-controlled reaction system that generates an active FLP species comprising **B[13]** and THF was extensively applied to the reductive alkylation of multisubstituted aniline derivatives. However, the direct use of amino acids was still found to be challenging even under harsh reaction conditions.[32] Meanwhile, Soós and co-workers constructed a substrate-controlled system, that furnishes an FLP from $B(2\text{-Cl-6-FC}_6H_3)(2,6\text{-}Cl_2C_6H_3)_2$ and *in situ* generated imine intermediates, which was predominantly applied to the functionalization of *N*-alkyl amines.[7] To further expand the utility of such BAr_3-catalyzed reductive functionalization methods using H_2, Hoshimoto and co-workers recently demonstrated an *in silico* assisted strategy to significantly shorten the lengthy trial-and-error processes usually used for the optimization of BAr_3 (Scheme 9).[33] In this study, **B[29]**–**B[38]** were prepared for the construction of an *in silico* library of BAr_3 for the collection of the experimental parameters required for machine learning. Eventually, the optimal reaction system was discovered to be **B[34]** and 4-methyltetrahydropyran (MTHP) and this was successfully applied to the reductive alkylation of aniline-based amino acids and C-terminal-protected peptides.

Recently, Hoshimoto and co-workers also disclosed a conceptually novel approach for the direct use of 'crude' H_2 (a gaseous mixture of H_2, CO, CO_2, and/or CH_4) for the catalytic hydrogenation of unsaturated molecules (Scheme 10a).[8–10] Given that a huge amount of H_2 will be produced

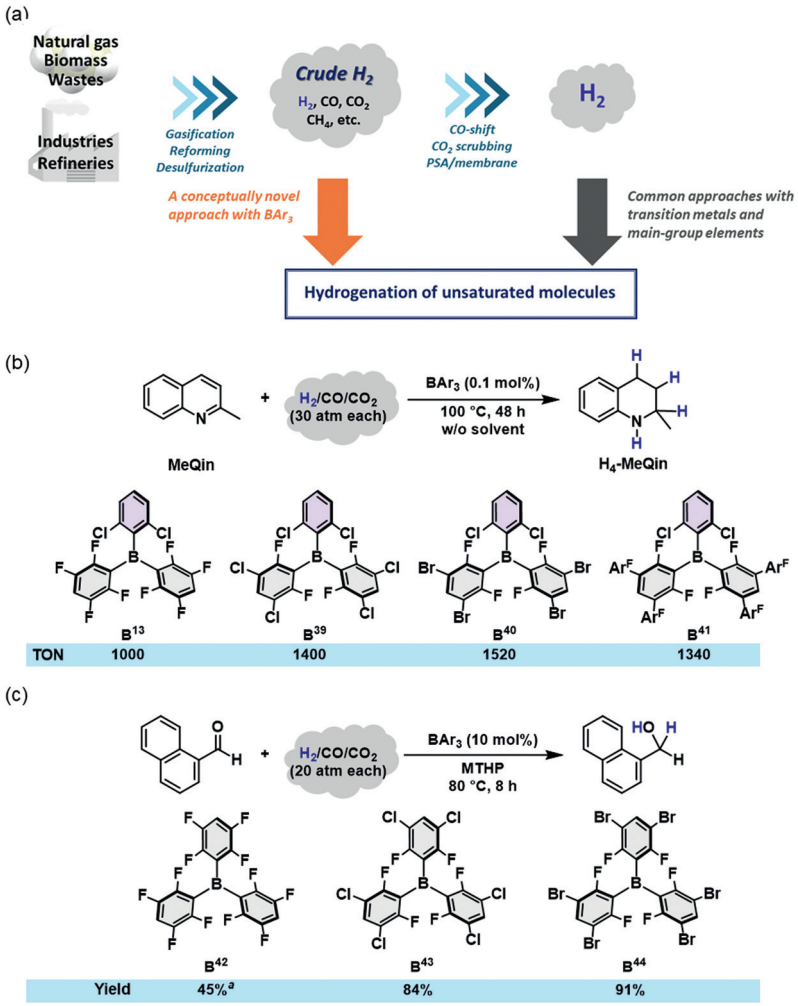


Scheme 9 (a) Heteroleptic BAr_3 species $\mathbf{B^{29}}$–$\mathbf{B^{38}}$ designed for the machine-learning-assisted optimization of borane catalysts and (b) $\mathbf{B^{34}}$-catalyzed reductive alkylation of amino acids and peptides using H_2. [a] 60 atm H_2; MTHP = 4-methyltetrahydropyran.

through the production of crude H_2 from hydrocarbon resources (i.e., natural gas, biomass, or food waste), the development of a technology bypassing the energy- and cost-intensive multistep purification processes of crude H_2 will be valuable.[34] The authors found that the hydrogenation of 2-methylquinoline (**MeQin**), used as a model liquid organic hydrogen carrier (LOHC), proceeded in the presence of 0.1 mol% of $B(2,6\text{-}Cl_2C_6H_3)(2,6\text{-}F_2\text{-}3,5\text{-}X_2C_6H)_2$ [X = F ($\mathbf{B^{13}}$), Cl ($\mathbf{B^{39}}$), Br ($\mathbf{B^{40}}$), and Ar^F ($\mathbf{B^{41}}$)] under solvent-free conditions.

The catalyst turnover number (TON) increased in the order $\mathbf{B^{13}}$ (1000) < $\mathbf{B^{41}}$ (1340) < $\mathbf{B^{39}}$ (1400) < $\mathbf{B^{40}}$ (1520) (Scheme 10b).[8] It should be noted here that the intrinsic Lewis acidity of $\mathbf{B^{13}}$, $\mathbf{B^{40}}$, and $\mathbf{B^{41}}$ is nearly identical, and thus, such a significant difference in TON should be attributed to the size of the *meta*-substituents (e.g., the degree of their remote back strain). $\mathbf{B^{40}}$ and $\mathbf{B^{41}}$ were also applied to the catalytic hydrogenation of 2,6-lutidine in the presence of gaseous mixtures of H_2/CO (40/4 atom each) and H_2/CO_2 (40/4 atom each) to afford 2,6-dimethylpiperidine. Finally, by taking advantage of the catalytic activity of $\mathbf{B^{41}}$ in the dehydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline ($\mathbf{H_4}$**-MeQin**), the authors demonstrated a molecular-based H_2 purification via the hydrogenation of **MeQin** with crude H_2 and the subsequent dehydrogenation of $\mathbf{H_4}$**-MeQin** to afford highly pure H_2. Subsequently, Hoshimoto and co-workers also demonstrated that $\mathbf{B^{20}}$ could be successfully applied to the catalytic hydrogenation of unsubstituted quinoline under mixed gas ($H_2/CO/CO_2$) conditions.[9]

The aforementioned approach for the direct use of crude H_2 has recently been expanded to the catalytic hydrogenation of carbonyl compounds. In this case, a BAr_3 compound of the type, $B(2,6\text{-}F_2\text{-}3,5\text{-}X_2C_6H)_3$, was used, and the



Scheme 10 (a) Simplified schemes of typical contemporary routes for H_2 purification for the hydrogenation of unsaturated compounds; (b) direct use of crude H_2 for the catalytic hydrogenation of **MeQin** using **B**[13] and **B**[39]–**B**[41]; and (c) direct use of crude H_2 for the catalytic hydrogenation of 1-naphthaldehyde using **B**[42]–**B**[44]. [a] 1,4-Dioxane used as the solvent.

alcohol yield was found to increase when the *meta*-substituents were changed from X = F (**B**[42]) to Cl (**B**[43]) to Br (**B**[44]) (Scheme 10c).[10] Notably, this trend in reaction efficiency is consistent with the increase in the E_{DEF} values. Therefore, the increased remote back strain seems to provide higher reaction efficiency by preventing the formation of an adduct with the LBs involved in the system. Importantly, the formyl groups in the aromatic and aliphatic aldehydes that also contain halogen and olefinic substituents can be selectively hydrogenated under mixed gas conditions. Furthermore, **B**[44] catalyzed the hydrogenation of undec-10-enal in the presence of a gaseous mixture of H_2, CO, CO_2, and CH_4 (76/0.2/20/3.2 molar ratio), which is produced from CH_4 via desulfurization, stream reforming, and CO-shift conversion processes in industry. These examples showcase (i) the power that can be extracted from BAr_3 catalysis via the fine-tuning of their Lewis acidity based on *meta*-substitution and (ii) the advantages of BAr_3 relative to the simple alternative of transition metal catalysts that require the use of purified H_2.

2.3 Other Examples of *meta*-Functionalization of BAr_3

The introduction of Mes groups into BAr_3 can significantly increase their stability toward LBs such as H_2O. For example, in 1960, B(2,4,6-Me_3-3,5-$(NO_2)_2C_6)_3$ (**B**[45]) was prepared by treatment of $B(Mes)_3$ with a mixed acid under cryogenic conditions (Figure 4).[35] Later, Ashley, Wildgoose, Slootweg, and co-workers used **B**[45] to accomplish the homolytic H_2 cleavage through a one-electron reduction in the absence of an external Lewis base.[36] In 1981, Wilson and co-workers reported the synthesis of B(3-$MeOC_6H_4$)(2,4,6-

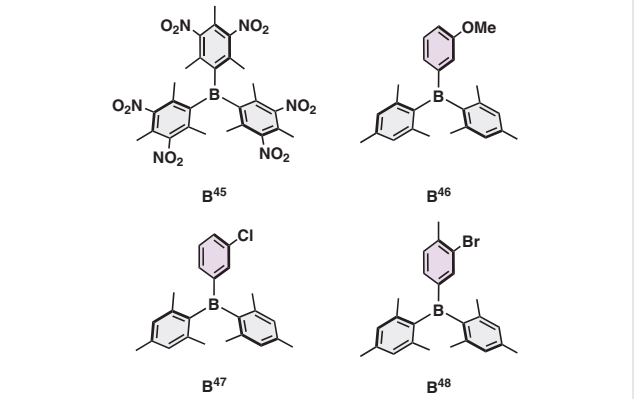


Figure 4 *meta*-Substituted BAr_3 **B[45]–B[48]** with 2,4,6-Me_3-aryl units.

$Me_3C_6H_2)_2$ (**B[46]**) and B(3-ClC_6H_4)(2,4,6-$Me_3C_6H_2)_2$ (**B[47]**).[37] More recently, Ito and co-workers demonstrated the synthesis of B(3-Br-4-MeC_6H_3)(2,4,6-$Me_3C_6H_2)_2$ (**B[48]**) via the reaction between 2,4-dibromo-1-methylbenzene and Ph_2MeSi–$BMes_2$ in the presence of Na(O^{t}Bu).[38]

3 Conclusions and Perspectives

This Short Review summarizes previously reported *meta*-substituted triarylboranes (BAr_3) and classifies them based on the roles that the *meta*-substituents, with respect to the boron centers, on the aryl groups play. The electronic and steric effects imparted by the *meta*-substituents have been used to tune the electronic/physical properties and reactivity of BAr_3 with respect to Lewis bases (i.e., the Lewis acidity). The introduction of electron-donating or -withdrawing groups at the *meta*-positions can change the intrinsic electrophilicity (e.g., the energy level of the empty p orbital of the boron center and the charge) of the boron atoms. A buttressing effect caused by a *meta*-substituent that pushes an adjacent *ortho* group closer to the boron atom has also been discussed. Importantly, recent progress in theoretical calculations has enabled the detailed consideration of non-covalent interactions (NCIs) related to the aryl *meta*-substituents. In this context, regulation of the stability of (pre-organized) Lewis adducts by London dispersion energies and remote back strain can be taken into consideration.

It should be noted here that the substitution of the *ortho*- and/or *para*-positions significantly impacts the reactivity of BAr_3 by modulating the intrinsic electrophilicity and front strain (intermolecular repulsion caused by the *ortho*-substituents). After such a relatively rough modulation, fine-tuning the Lewis acidity via *meta*-substitution should work better and eventually play a critical role in affording a desired reactivity to BAr_3. In fact, *meta*-designed BAr_3 compounds have been applied in challenging catalytic molecular transformations, such as reductive alkylation of valuable amines (including amino acids and peptides), as well as molecular-based H_2 purification systems. However, the preparation of BAr_3 species with unprecedented substitution patterns is typically laborious and time-consuming when one attempts it for the first time. Thus, cheminformatics-based prediction and optimization of the target BAr_3 will likely be an area of future research.[33,39,40] The authors anticipate further diversification of the structures and applications of BAr_3 through their *ortho*-, *para*-, and *meta*-functionalization. Given there are a maximum of six slots for each *ortho*- and *meta*-position in a single triarylborane molecule, along with three slots for the *para*-position, the exploration of BAr_3 will continue.

Conflict of Interest

The authors declare no conflict of interest.

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