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Review

Boron-Based Lewis Acid Catalysis: Challenges and Perspectives

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Abstract: In the last two decades, boron-based catalysis has been gaining increasing traction in the field of organic synthesis. The use of halogenated triarylboranes as main group Lewis acid catalysts is an attractive strategy. It has been applied in a growing number of transformations over the years, where they may perform comparably or even better than the gold standard catalysts. This review discusses methods of borane synthesis and cutting-edge boron-based Lewis acid catalysis, focusing especially on tris(pentafluorophenyl)-borane [$B(C_6F_5)_3$], and other halogenated triarylboranes, highlighting how boron Lewis acids employed as catalysts can unlock a plethora of unprecedented chemical transformations or improve the efficiency of existing reactions.

Keywords: boron; boranes; tris(pentafluorophenyl)borane; Lewis acid; catalysis

1. Introduction

Boron reagents are often employed as Lewis acids because of their strong electrophilic nature by virtue of a vacant p-orbital which can readily accept electrons from donor molecules. Many boranes have been synthesised and employed over the years, including trialkyl-, triaryl- and trihalo-boranes. As the field of boron chemistry was growing, the variety of boron reagents grew along. In fact, over the years, a series of boron-based catalysts of tunable acidity and increasing structural complexity arose (Figure 1a) [1]. One of the most interesting examples are boron trihalides BX_3 (X = F, Cl). Although they are exceptionally efficient as catalysts, they are extremely moisture-sensitive and, additionally, its volatile nature makes them difficult to handle. In the 1950s, investigations were carried out on perfluoroalkyl boranes, whose highly electronegative fluorinated ligands confer strong Lewis acidity to the boron centre and the B–C bonds were expected to be less hydrolytically sensitive. However, perfluoroalkylboranes exhibit thermal instability [2]. Therefore, the focus was shifted on halogenated triarylboranes, such as tris(penta-fluorophenyl)-borane [$B(C_6F_5)_3$], commonly known as BCF, which was first synthesised in the 1960s by Massey (Figure 1b) [3,4]. Although the scientific community was aware of its interesting Lewis acid properties, the field remained dormant until it was used as initiator in the polymerisation of olefins with metallocenes [5–10]. Few years later it gained further attention since Piers discovered its capability to catalyse hydrosilylation reaction of carbonyl compounds [11]. In 2006, BCF received a new momentum thanks to Stephan's finding that boranes bearing halogenated aryl groups can form with phosphines an adduct named "frustrated Lewis pairs" (FLPs), able to activate small molecules, such as H_2 and CO_2, for example [12,13]. This review highlights recent reports of emergent boron chemistry, beginning by examining new methodologies for the synthesis of novel Lewis acidic boranes, to highlight how this field has grown in the last few years. Finally, examples on the use of boron-based catalysts will also be discussed. The focus of the review is on the most recent examples, although some historical examples are included to provide the reader with a better overview.

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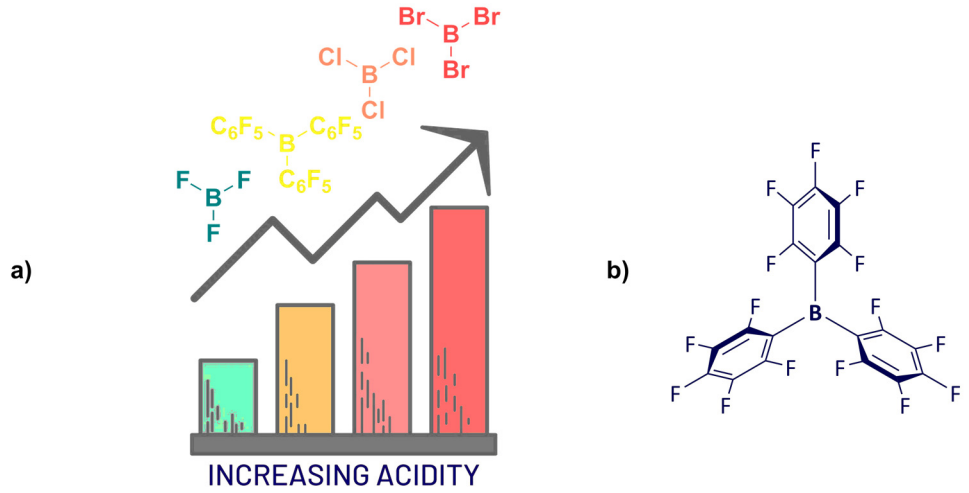
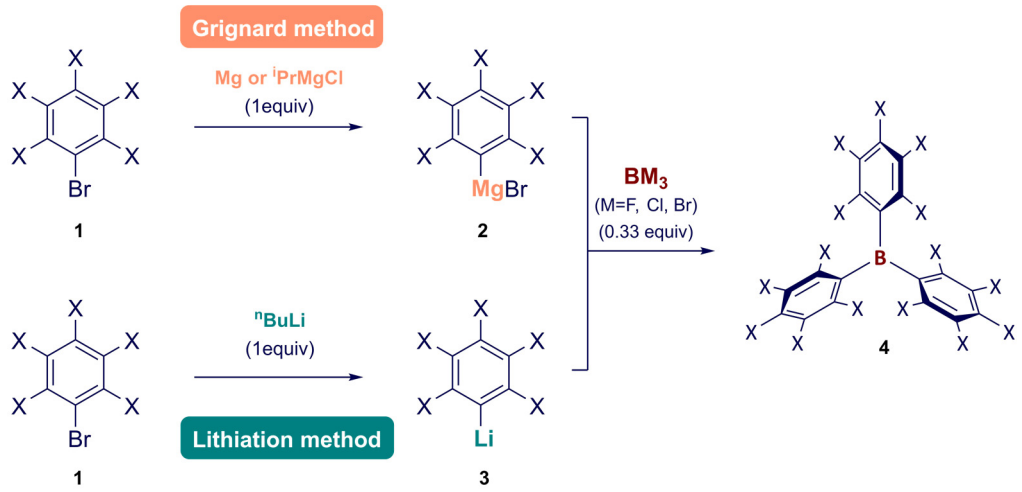


Figure 1. (**a**) Visual representation of the scale of increasing acidity of different boron-based Lewis acids; (**b**) Tris(pentafluorophenyl)-borane (BCF).

2. Synthesis

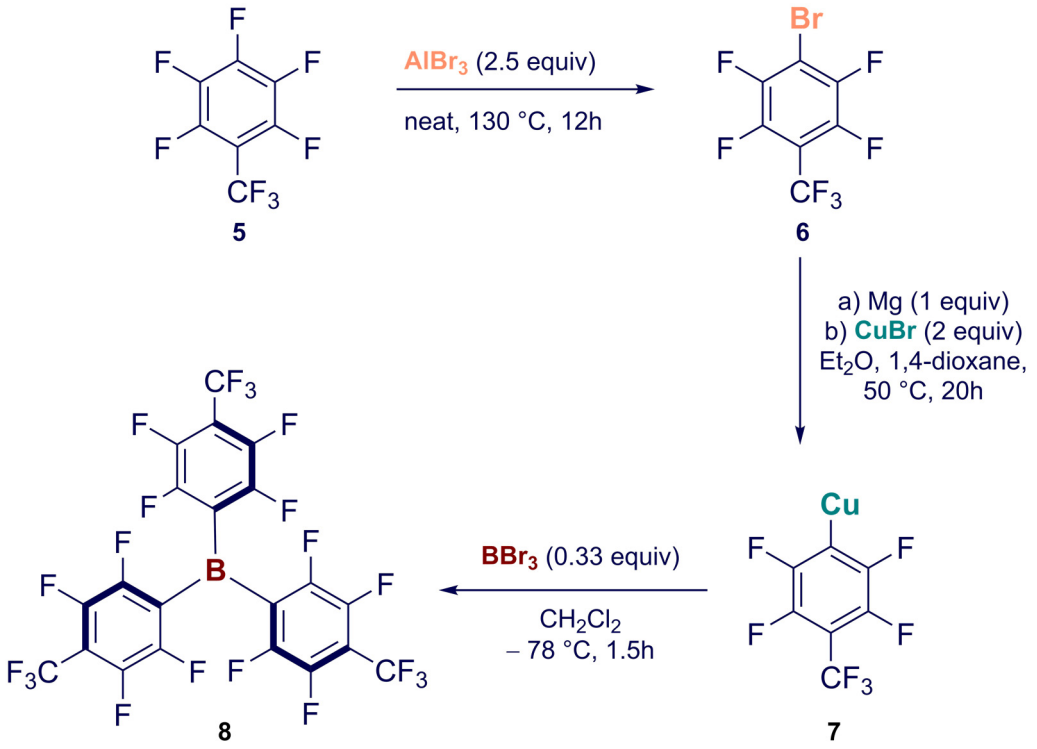
Synthesis of Homoleptic and Heteroleptic Halogenated Triarylboranes

Homoleptic halogenated triarylboranes can be synthesised in two ways: either via the Grignard method or the lithiation method. In 1963 Massey and coworkers first described the synthesis of BCF using a Grignard reagent with BCl_3 [3] later, whereas the lithiation procedure was reported in the patent literature in 1994 [14]. General procedures are both shown in Scheme 1. To obtain the desired product in higher yields, modifications and different purification strategies have been adopted. $B(2\text{-}FC_6H_4)_3$, $B(4\text{-}FC_6H_4)_3$, $B(2,6\text{-}F_2C_6H_3)_3$, $B(2,4,6\text{-}F_3C_6H_2)_3$, $B(3,4,5\text{-}F_3C_6H_2)_3$, and $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ have been synthesised employing the Grignard method with subsequent purification (sublimation) [15–19]. Boranes with trifluoromethyl groups on the aryl ring, $B(2,4\text{-}(CF_3)_2C_6H_3)_3$, $B(2,5\text{-}(CF_3)_2C_6H_3)_3$, $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ and $B(2\text{-}(CF_3)C_6H_4)_3$ have been prepared by the lithiation method [20–22]. Bulkier analogues of BCF, e.g., $[B(C_{10}F_7)_3]$ and tris(perfluorobiphenyl) borane $[B(2\text{-}(C_6F_5)C_6F_4)_3]$, have also been synthesised by the lithiation method [23,24].



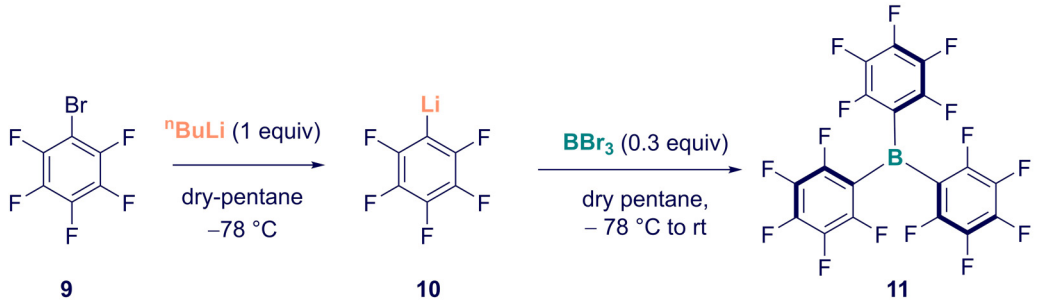
Scheme 1. Different routes to synthesise homoleptic halogenated triarylboranes.

The synthesis of the tris(perfluorotolyl)borane $[B(4\text{-}(CF_3)C_6F4)_3]$ **8** was shown by Mitzel and coworkers using a Grignard reagent to prepare an arylcopper intermediate **7** as shown in Scheme 2 [25]. The copper intermediate underwent a transmetallation reaction with BBr_3 to generate the desired borane **8**.



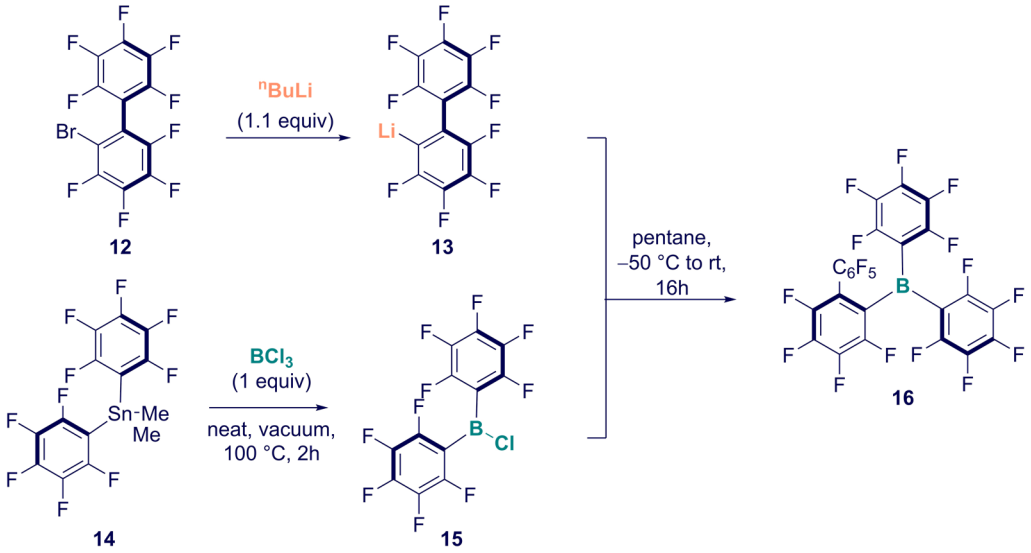
Scheme 2. Synthesis of the tris(perfluorotolyl)borane [B(4-(CF_3)C_6F_4)$_3$] **8**.

The synthesis of BCF **11** was carried out for the first time by Massey et al. by preparing it in pentane, since boron compounds normally complex readily with ethers and make isolation of the desired product much more difficult (Scheme 3) [3].



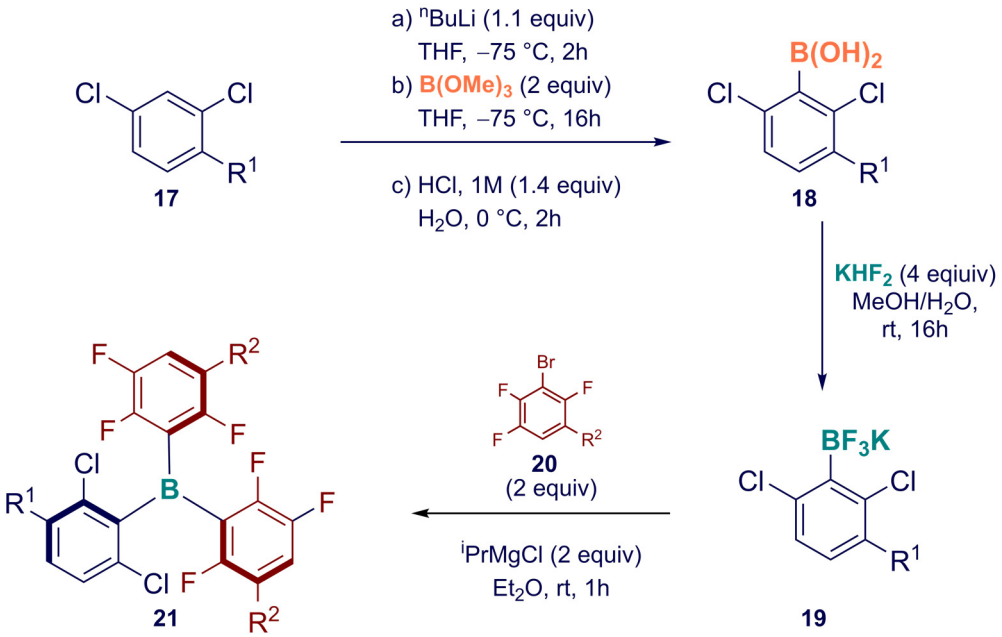
Scheme 3. Synthesis of BCF **11**.

Whilst the Lewis acidity and catalytic activity of halogenated triarylboranes can be tuned by varying the number of halogen atoms and their position on the aryl rings, further fine-tuning is possible through the synthesis of heteroleptic boranes. Few heteroleptic boranes have been synthesised because of the complexity of the procedures; the synthesis of B(C_6F_5)$_2$(2-(C_6F_5)C_6F_4) is probably the simplest heteroleptic borane: it was prepared replacing one perfluorophenyl moiety with a perfluorobiphenyl motif. The synthetic procedure for preparing the 2-bromononofluoro-biphenyl portion involves the reaction of (C_6F_5)Li and C_6F_5Br. Then, the addition of BCl_3 to Sn(Me)$_2$(C_6F_5)$_2$ **14** generated the B(C_6F_5)$_2$Cl **15**. Finally, the reaction between the two partners, B(C_6F_5)$_2$Cl **15** and 2-lithiumnonofluorobiphenyl **13**, afforded B(C_6F_5)$_2$(2-(C_6F_5)C_6F_4) **16** as shown in Scheme 4 [26].



Scheme 4. Synthesis of one of the simplest heteroleptic borane: $B(C_6F_5)_2(2\text{-}(C_6F_5)C_6F_4)$ **16**.

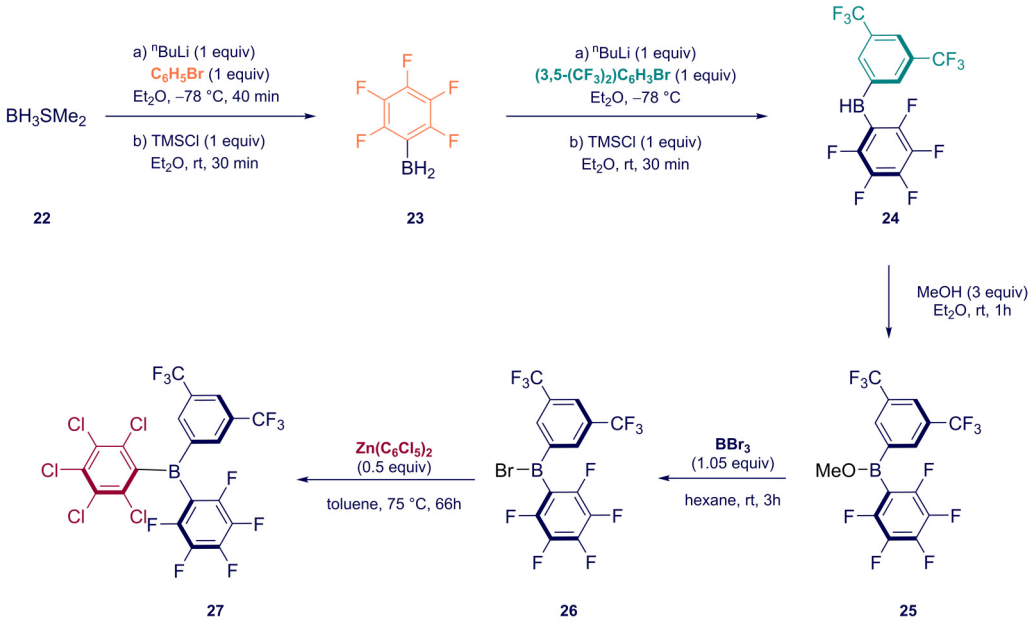
Soós research group performed the synthesis of other interesting heteroleptic boranes bearing chlorinated and fluorinated aryl rings **21** as shown in Scheme 5. The dihalobenzene derivatives **17** were reacted with n-butyl lithium and trimethyl borate, affording boronic acids **18**. They were then converted into the potassium trifluoroborate salt **19**, that could be reacted with Grignard reagents bearing different aryl frameworks to form the desired heteroleptic boranes. These boranes have the great advantage of being moisture tolerant thanks to the steric hindrance of the chlorine atoms which prevent water from binding to the boron centre [27].



Scheme 5. Synthetic route for heteroleptic boranes bearing chlorinated and fluorinated aryl rings.

The first example of halogenated triarylborane bearing three different aryl rings, $B(C_6F_5)(C_6Cl_5)(3,5\text{-}(CF_3)_2C_6H_3)$ **27**, was synthetised from borane dimethylsulfide **22** through five synthetic steps. First, a single equivalent of $Li(C_6F_5)$ was generated at −78 °C and was reacted with borane dimethylsulfide **22** to form $[H_3B(C_6F_5)]$. The excess hydride was abstracted with TMSCl obtaining $H_2B(C_6F_5)$ **23**. The trifluoromethyl bearing aryl ring was installed via a similar strategy by adding $Li(3,5\text{-}(CF_3)_2C_6H_3)$ and abstraction of the excess

hydride by TMSCl. The resulting $HB(C_6F_5)(3,5\text{-}(CF_3)2C_6H_3)$ **24** was reacted with excess methanol and then BBr_3 to form $BrB(C_6F_5)(3,5\text{-}(CF_3)C_6H_3)$ **26**. Finally, the bromoborane was reacted with half an equivalent of $Zn(C_6Cl_5)_2$ to install the last aryl ring, by affording the desired heteroleptic borane **26** (Scheme 6) [28].



Scheme 6. Synthesis of $B(C_6F_5)(C_6Cl_5)(3,5\text{-}(CF_3)_2C_6H_3)$.

3. Catalysis

Main group catalysis found fertile soil in carbon–carbon bond forming reactions, hydrogenation, hydroboration and many other transformations, which are traditionally achieved by metal-based catalysis. Even if this field remained dormant for a long time, mainly because of the aforementioned technical difficulties, once those were overcome, the main group catalysis progressed quickly, leading to the development of a wide range of novel and mild strategies to perform the classical chemical transformations. The key advantages of employing main-group elements in catalysis is their generally lower cost, which makes them more attractive to industry, and their lower toxicity compared with heavy-metals. The current focus of many research groups involves the development of new methodologies to make catalysis "greener". Using earth-abundant, less toxic, first-row transition metals, chemists are re-examining well known strategies to make them more environmentally-friendly [29–31]. Boron-based compounds are widely employed as main group catalysts: boronic acids prominently for the activation of hydroxy functional groups [32], doubly B-doped (hetero)arenes as activators of p-block molecules [33], and boranes capable of activating a large number of substrates via a variety of transformations (Figure 2). While boronic acids and doubly B-doped (hetero)arenes are extensively employed in organic synthesis, boranes catalysis is a less developed field. Boranes can act as Lewis acid catalysts thanks to their empty p-orbital on the central boron atom. The basis for boranes-mediated Lewis acid catalysis is led by the attack and subsequent release of their empty p-orbital. BCF is probably the catalyst that has received most of the attention, as it will be evident from the following examples. An additional advantage in terms of acidic nature of BCF is given by the three electron-deficient pentafluorophenyl rings directly bonded to the boron centre, placing the Lewis acidity of BCF between the ones of $BF_3{\cdot}Et_2O$ and BCl_3. Moreover, the catalytic reactivity of BCF is enhanced by the fluorine atoms of the pentafluorophenyl ring, which are able to interact with substrates via hydrogen bonding or other electrostatic interactions. The pentafluorophenyl rings provide extra bulkiness to the BCF, which inhibits the formation of the classical Lewis acid–base adduct. Another strong point for its use as catalyst is its high thermal stability. This property makes it suitable for

high-temperature reactions that can easily rival transition metal catalysts [2,34–37]. This versatile catalyst also possesses the ability to coordinate with lone pair of heteroatoms, that promotes various defunctionalisation reactions as well as valuable functional groups incorporation via a new C–C or C–heteroatom bond.

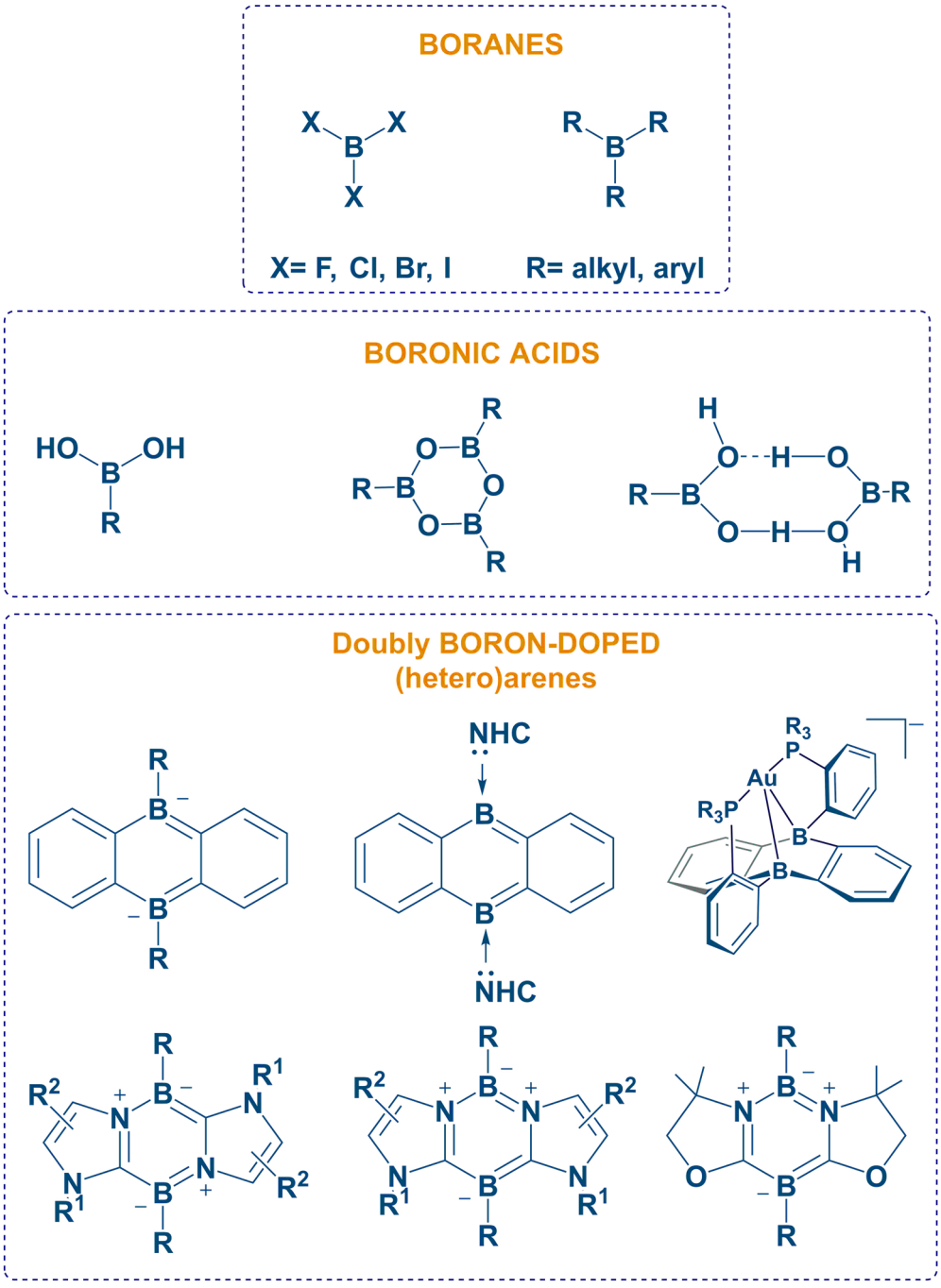


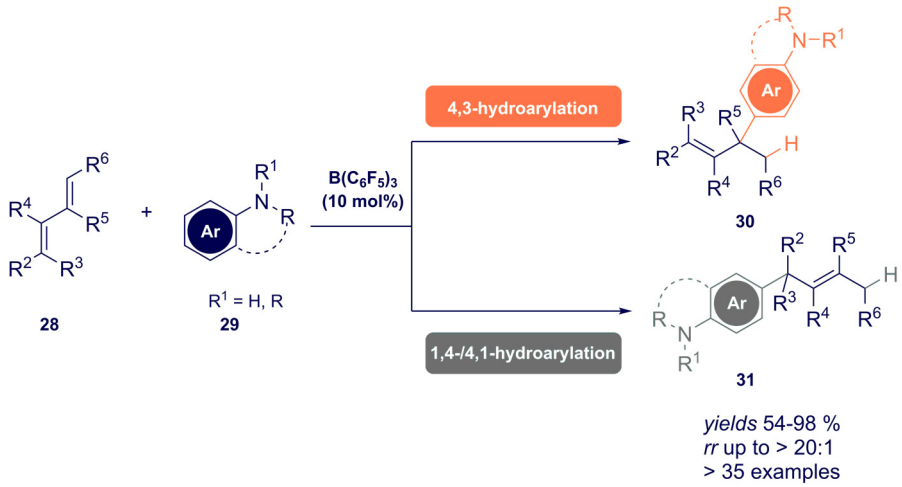
Figure 2. Different classes of boron-based catalysts.

In the following sections, representative ground-breaking examples in this field over the last five years will be discussed.

3.1. Boron-Based Catalysis

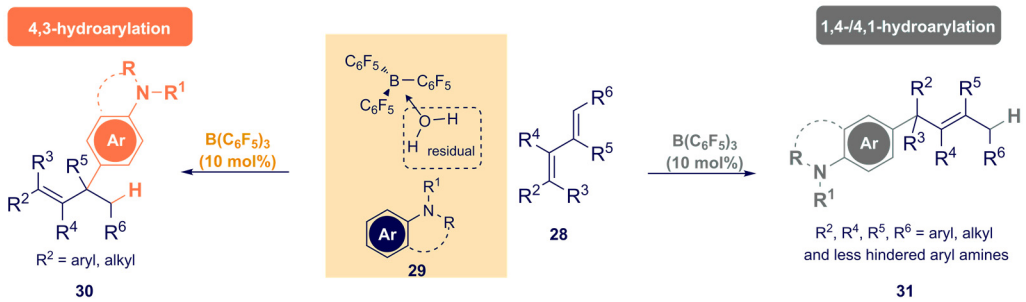
Recently BCF-catalyzed reactions have given renaissance to several chemical transformations. In this regard, a ground-breaking example come from Chatterjee's research group by performing hydroarylation reactions of conjugated dienes **28** under mild reaction

conditions. This novel strategy developed a broad substrate scope of sterically hindered aniline derivatives **29** via highly regioselective functionalisation driven by BCF catalysis (Scheme 7).



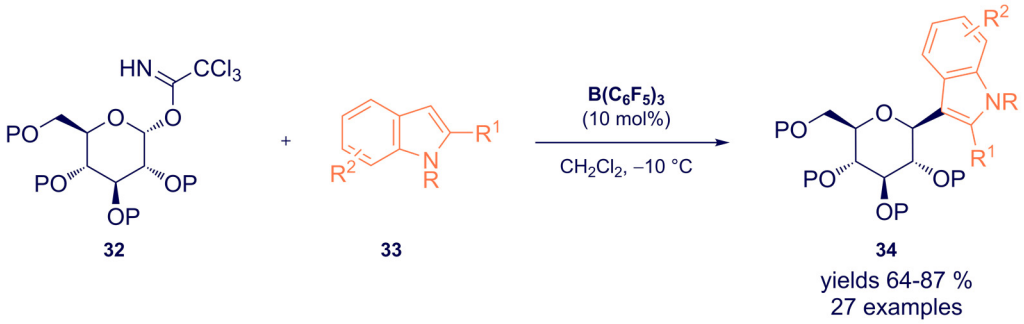
Scheme 7. Hydroarylation reactions of conjugated dienes via BCF catalysis.

Aniline derivatives **29**, in particular diarylamines, are essential structural motifs that have variety of applications, such as in medicinal chemistry, agrochemical or pharmaceutical industry, and natural products. That is why the development of an efficient route for the synthesis of diarylamines and their derivatives is attractive [38]. This approach shows a wide substrate scope (>35 examples) with good functional group tolerance. The desired products are obtained with good to excellent yields (up to 98%) and high regioselectivity (*rr* up to >20:1). Chatterjee and coworkers showed that less hindered or alkyl-substituted arylamines mainly undergo 4,1- rather than 4,3-hydroarylation. With 1-aryl substituted dienes the 4,3-hydroarylation occurs, while 1-alkyl-substituted dienes mainly provided either 4,1- or 4,3-hydroarylated products, and 2-alkyl-substituted dienes mainly provided 1,4-hydroarylated compounds. Interestingly, the 1,2-, 1,4-, 4,1- or 4,3-hydroarylation take place depending on the nature of the substituents. To gain a deeper mechanistic insight, the Lewis acid catalyst BCF together with the residual water play a crucial role in the protonation of 1,3-dienes **28**, by converting it into the respective allyl cation intermediates inducing the facile electrophilic aromatic substitution of aniline substrates **29** (Scheme 8).



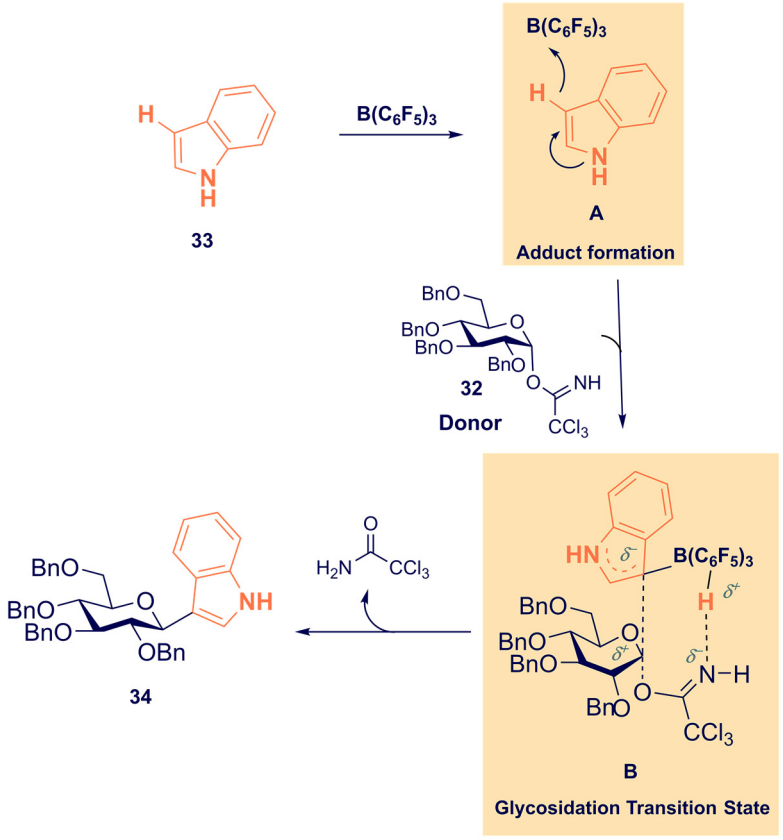
Scheme 8. Mechanistic insight in the hydroarylation reactions of conjugated dienes via BCF catalysis.

Moreover, BCF efficiently catalyses highly regioselective glycosidation reaction of indoles. This attractive approach has been recently developed by Mandal et al. coupling the glycosyl trichloroacetimidates **32** with a wide range of substituted indoles **33** in the presence of catalytic amounts of BCF (Scheme 9) [39].



Scheme 9. BCF catalysed regioselective strategy to access 3-indolyl-C-glycosides **34**.

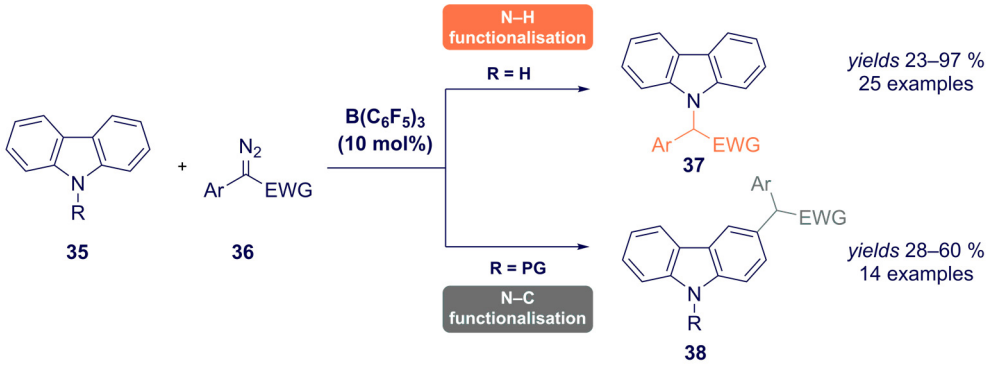
The authors have successfully developed an efficient stereoselective C-glycosylation protocol involving trichloroacetimidate glycosyl donors **32** with indoles **33**. The desired products **34** were obtained in good to excellent yields with mild and practical reaction conditions, in fact either molecular sieves or extremely low temperatures were required. The mechanism is elucidated in the Scheme 10: instead of performing a simple SN2-type mechanism the BCF undergoes an acid−base-type reaction. The nucleophilic acceptor **33** forms a complex with the catalyst (intermediate **A**), which ignite the perbenzylated α-glucosyl imidate donation (intermediate **B**).



Scheme 10. Mechanistic insight in the β-stereoselective 3-indolyl-C-glycosidation reaction.

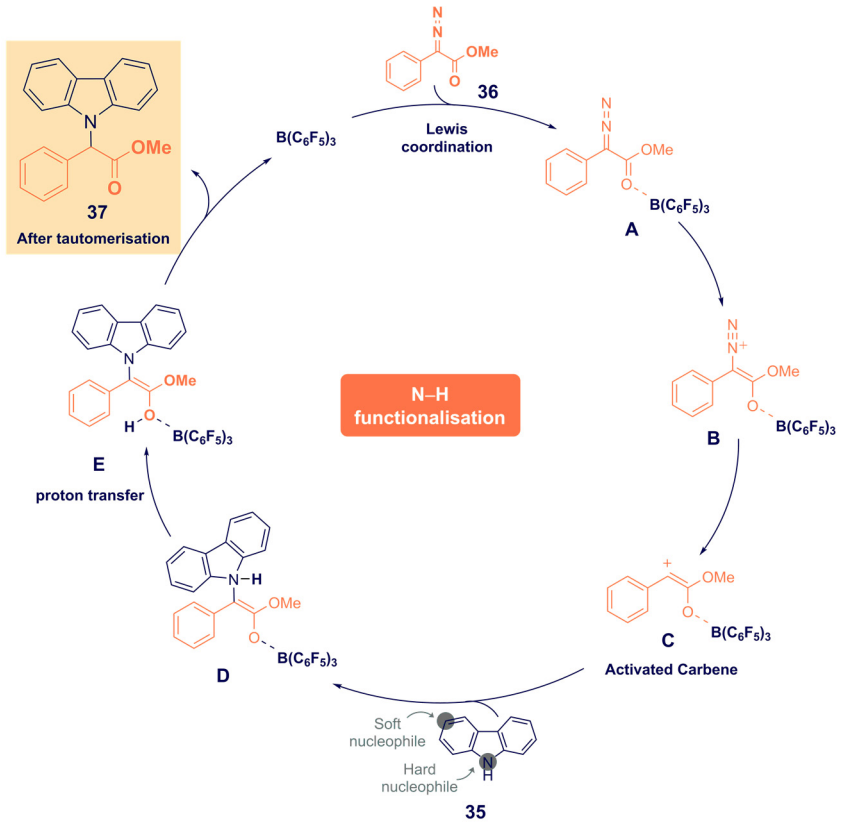
Recently Koenings et al. reported a BCF-catalyzed reaction of carbazoles **35** with aryldiazoacetates **36** (Scheme 11). Finely controlling the regioselectivity of this process is its inherent challenge: in fact, both N−H and C−H functionalisation can occur. In the case of unprotected carbazoles, only the N-H functionalization occurs. On the other hand, protected carbazoles undergo C−H functionalization at the C-3 position in good yields [40] The successful development of a regioselective method to functionalise carbazoles overcame

the need for metal catalysts in such transformations and demonstrated the important advances in the field of Lewis acid catalysis.



Scheme 11. BCF-catalysed reaction of carbazoles **35** with aryldiazoacetates **36**.

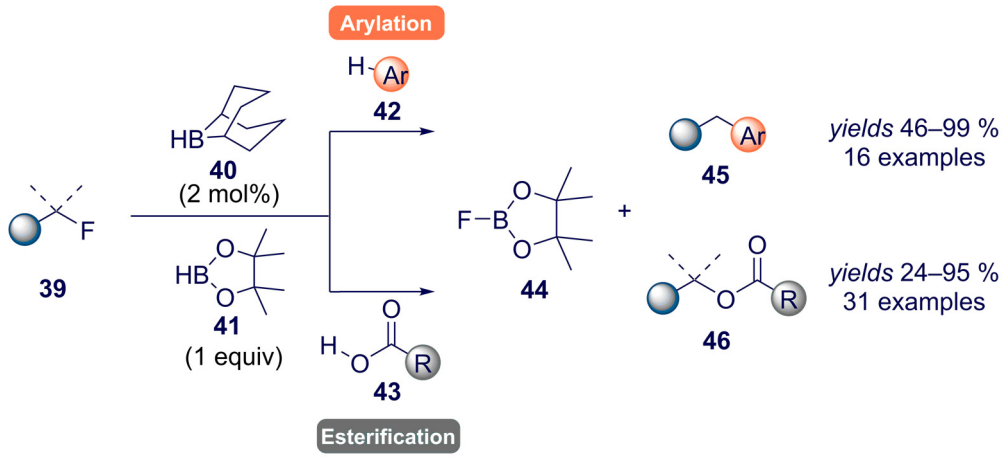
In the presence of BCF as a catalyst, a variety of carbazoles **35** functionalisation occurs with good to excellent yields (up to 97%) and high selectivity. From a mechanistic point of view (Scheme 12), BCF coordinates to the aryldiazoacetates **36**, generating a borane-stabilised vinyl cation or the activated carbene intermediate (the electrophilic intermediate **C**). The coordination to borane renders the intermediate **C** a hard intermediate, which reacts in the N−H functionalization of carbazole **35** following the hard and soft Lewis acids and bases principles. After the addition of carbazole **35**, the proton migration to the neighboring carbonyl group occurs giving rise to the intermediate **E**, which, upon tautomerization, releases the catalyst and provides the desired product **37**.



Scheme 12. Mechanistic perspective for the BCF-catalysed functionalisation of carbazoles **35**.

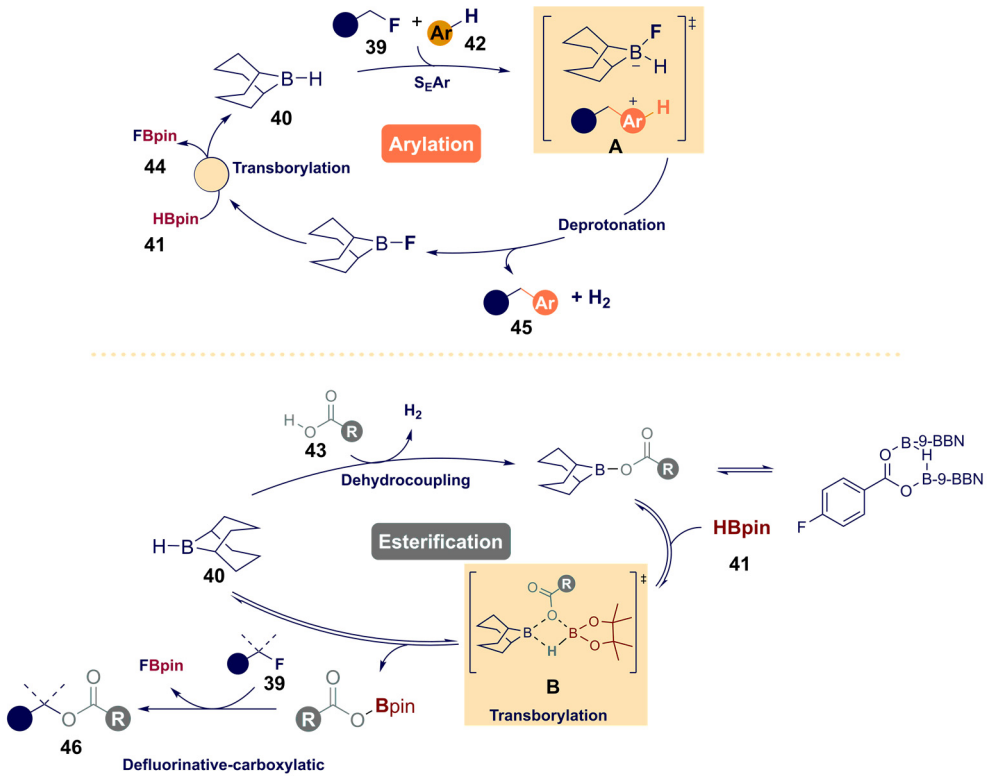
The activation and subsequent functionalization of carbon−fluorine bonds is highly synthetically demanding, because of the high thermodynamic barrier required to cleave

the C−F bond. Transborylation reaction is key to perform the borane catalyzed coupling of alkyl fluorides **39** with arenes **42** and carboxylic acids **43** (Scheme 13). Successful C−C and C−O bond formation across a variety of structurally and electronically differentiated arenes **42** and carboxylic acids **43** was obtained using 9-borabicyclo[3.3.1]nonane **40** (H-B-9-BBN) as catalyst and pinacolborane **41** (HBpin). Experimental and computational mechanistic studies elucidated how both transformations occur: B−F transborylation between F-B-9-BBN and HBpin **41** enabling catalytic turnover for C−C coupling. On the other hand, the exchange between the alkyl fluoride **39** and acyloxyboronic ester was proposed for C−O coupling, where H-B-9-BBN **40** catalysed the dehydrocoupling of the carboxylic acid **43** with HBpin **41** [41].



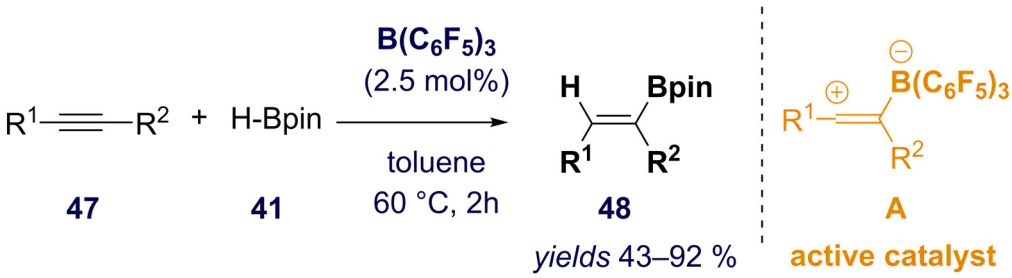
Scheme 13. Borane-catalyzed coupling of alkyl fluorides **39** with arenes **42** and carboxylic acids **43**.

This approach has been demonstrated with high functional group tolerance and high efficiency, furnishing the desired products in good to excellent yield (up to 99%). Mechanistic investigations shown in Scheme 14 confirmed that, regarding the C−F arylation, the dissociation of the borane dimer $[H\text{-}B\text{-}9\text{-}BBN]_2$ and the subsequent coordination to benzyl fluoride **39** initiate the carbon−carbon bond formation, by generating a carbocation and a fluoroborohyride by fluoride extraction. Then, the nucleophilic attack of the arene **42** to give a Wheland intermediate **A**, followed by deprotonation by the fluoroborohydride, generates the C−C coupled product **45**, releasing H_2. The catalytic turnover was ensured by F-B-9-BBN which undergoes B−F transborylation with HBpin **41** to give FBpin **44** and regenerates the H-B-9-BBN catalyst **40**. For C−F esterification, upon the formation of monomeric H-B-9-BBN **40**, rapidly the dehydrocoupling reaction with the carboxylic acid **43** occurs and the acyloxy-B-9-BBN is formed, while H_2 released. Acyloxy-B-9-BBN reversibly originated the corresponding H-B-9-BBN adduct. Reversible B−O transborylation with HBpin **41** yielded acyloxy-Bpin and regenerated the H-B-9-BBN catalyst **40**. The acyloxy-Bpin underwent C−F esterification with the alkyl fluoride **39** and gave the desired C−O coupled product **46** and FBpin **44**.



Scheme 14. Mechanistic elucidation for the BCF-catalyzed coupling of alkyl fluorides **39** with arenes **42** and carboxylic acids **43**.

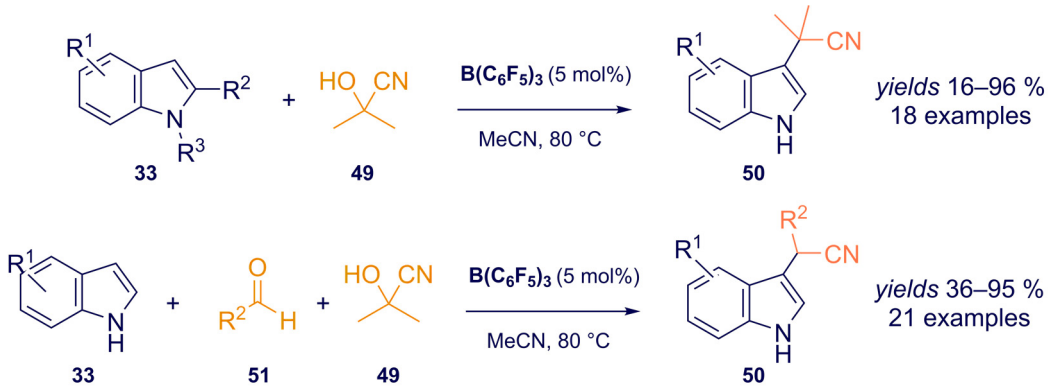
Similarly, the same research group employed a similar approach to improve the efficiency of well-known transformations via BCF catalysis [42]. They developed a protocol to perform the hydroboration of alkynes **47** and styrene with HBpin **41** using BCF as the initiator of catalysis (Scheme 15). In fact, a zwitterionic intermediate **A** is formed when BCF meets the alkyne moiety **47** and subsequently it acts as a catalyst for the desired reaction. This zwitterion is a strong enough Lewis acid to catalyse the hydroboration of alkenes, offering a promising methodology to explore further reactivity of the archetypal boron Lewis acid.



Scheme 15. BCF-catalyzed hydroboration of alkynes **47** and styrene.

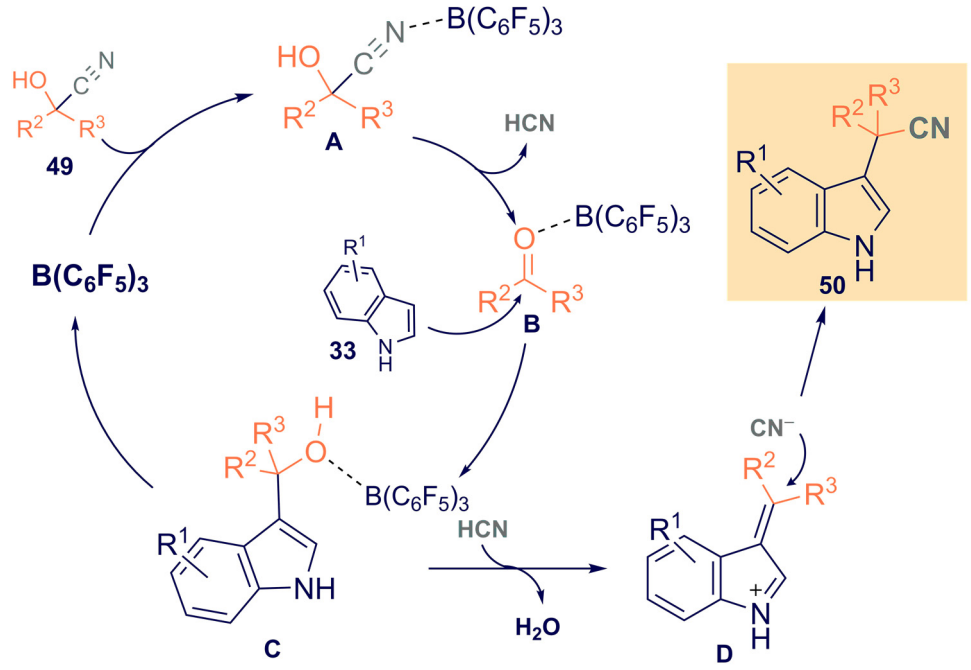
Despite the great achievements related to the C3 functionalization of indoles, cyanoalkylation reactions of this pharmacologically relevant moiety remain underinvestigated. Minakata's research group tackled this challenge by coupling cyanohydrins **49** with indoles **33** in the presence of a catalytic amounts of BCF (Scheme 16). Mechanistic studies revealed the unique reactivity of the BCF catalyst in coordinating the cyano group to the boron center to trigger the desired reaction. Another strength of this methodology is that it is a three-component reaction (using indoles **33**, aldehydes **51**, and acetone cyanohydrin **49**). This allows to circumvent the synthesis of each aldehyde-derived cyanohydrin separately.

The developed method provides straightforward and highly efficient route to produce various types of synthetically useful indole-3-acetonitrile derivatives **50** [43].



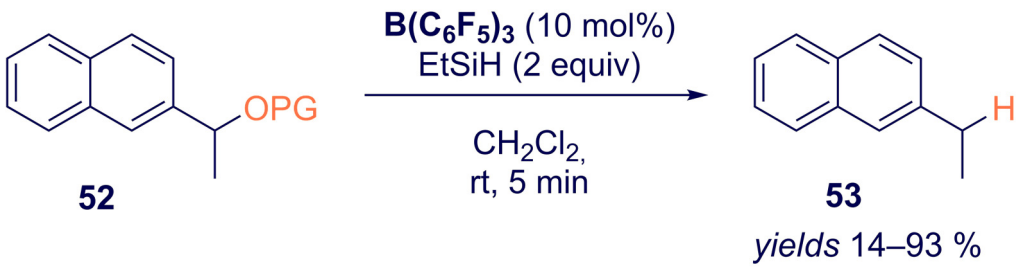
Scheme 16. Cyanoalkylation reaction of indoles mediated by BCF.

Based on the experimental results, Minakata and coworkers proposed the reaction mechanism reported in Scheme 17. First, the cyanohydrin **49** decomposed into HCN and the corresponding carbonyl compound thanks to the coordination of the cyano moiety to BCF. Subsequently, indole **33** attacks the resulting carbonyl compound, which is more reactive owing to BCF coordination, to form the alcohol intermediate **C**. This intermediate undergoes dehydration, leading to the formation of electrophilic iminium compound **D**. The cyanide generated through the dehydration step attack the electrophile generated in situ to afford cyanoalkylated product **50**. This reaction pathway highlights the unique catalytic activity of BCF that activates three different species in the same catalytic cycle: cyanohydrins, carbonyl compounds, and alcohol intermediate.



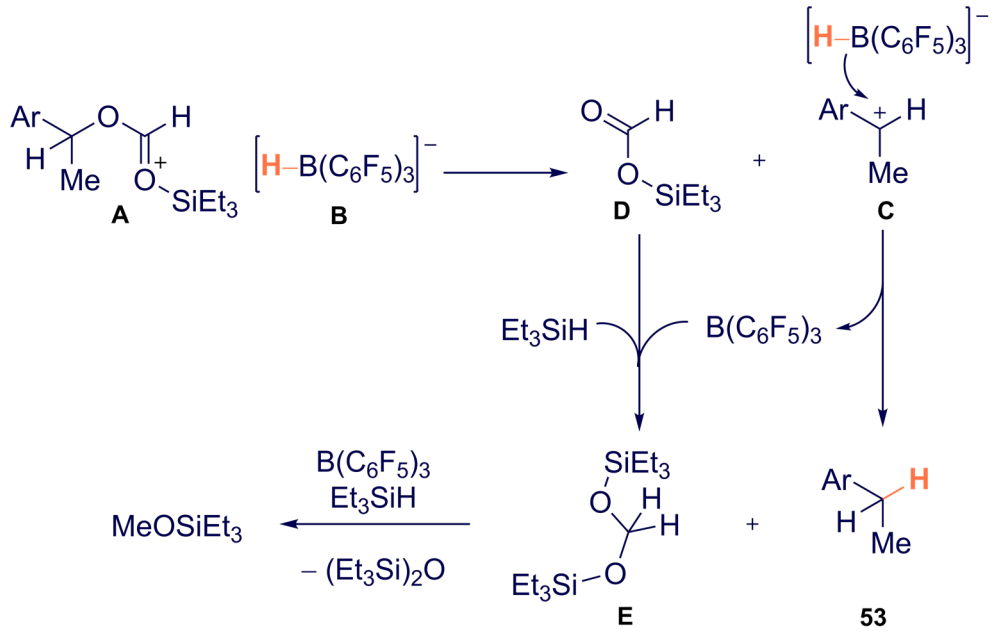
Scheme 17. Reaction mechanism proposed for the BCF-catalyzed cyanoalkylation reaction of indoles.

Oestreich's research group drew up a sequence of formylation and BCF-catalyzed reduction of the resulting formate with Et_3SiH enabling the chemoselective deoxygenation of secondary benzylic alcohols **52** (Scheme 18). The formyl group fulfills a dual role as activator and sacrificial protecting group. The limit of this methodology is that both primary benzylic and tertiary non-benzylic alcohols are not reduced by this protocol [44].



Scheme 18. BCF-catalyzed chemoselective deoxygenation of secondary benzylic alcohols **52**.

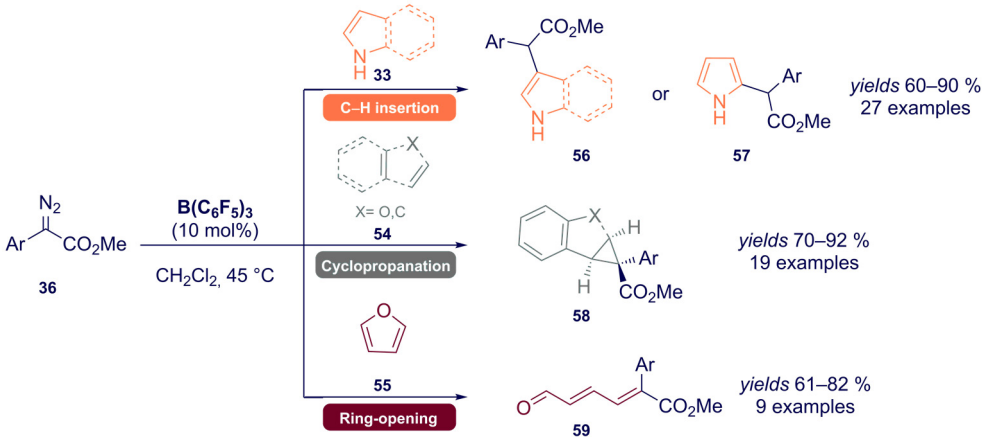
The desired products **53** were obtained in up to excellent yields (14–93%). The reaction under investigation was realised by a formylation followed by a subsequent BCF-catalysed reduction with Et_3SiH as shown in Scheme 19. At first, the primary formate converts into the silylcarboxonium ion **A** with the borohydride **B** as counteranion. Then, this intermediate is reduced to the acetal **E** which is further reduced to the silyl ethers and Et_3SiOMe which is finally reduced to methane. The deoxygenation of the secondary formate follows an SN_1 mechanism. Silylcarboxonium ion **A** dissociates into the benzylic carbenium ion **C** and the silylated formate **D**. The borohydride **B** transfers a hydride to the carbenium ion **C** affording the hydrocarbon. At the same time, the formate converts into bis-silyl acetal, silylated methanol, methane, and the disiloxane via BCF-catalyzed hydrosilylation.



Scheme 19. Mechanistic insights for the BCF-catalyzed deoxygenation of secondary benzylic alcohols **52**.

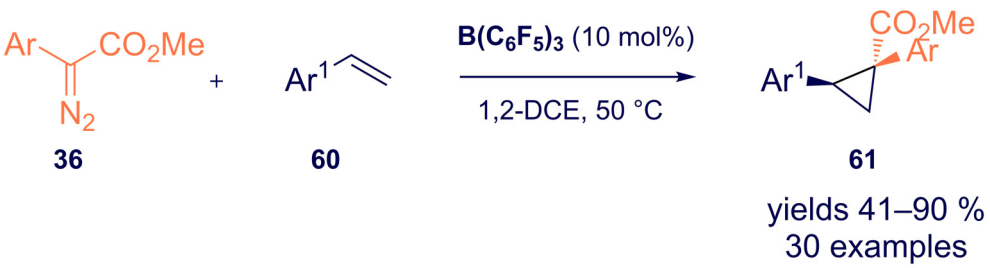
Over the last decades, the use of BCF was established as one of the privileged catalytic alternatives to form carbon–carbon bonds in the absence of precious transition metal catalysts. Melen's research group demonstrated the metal-free alkenylation reactions of aryl esters with α-diazoesters to obtain highly functionalised enyne derivatives (Scheme 20). Lewis acidic boranes have been shown to be valid catalysts for highly selective reactions of diazo compounds with a wide range of synthetic partners. The reactions of α-aryl α-diazoesters **36** with nitrogen heterocycles indole **33** or pyrrole selectively generate C3 and C2 C–H insertion products, respectively, in good to excellent yields even with unprotected indoles. Under the same mild condition α-aryl α-diazoesters **36**, benzofuran, indene, and alkene substrates **54** give exclusively cyclopropanation, whereas furans **55** lead to the ring-opening reaction. This simple and mild approach proved itself to be an effective alternative to the most commonly used protocols to access the reactions of α-aryl α-diazoesters **36**

with (hetero)cycles and alkenes [45]. This work shows the highly selectivity of the catalytic reactions of α-aryl α-diazoesters **36** with a wide range of (hetero)cycles and olefins via the activation of the diazocompounds thanks to BCF. Theoretical DFT calculations have been employed to deeply investigate the reaction mechanisms as well as the different regio- and diastereoselectivities of the substrates.



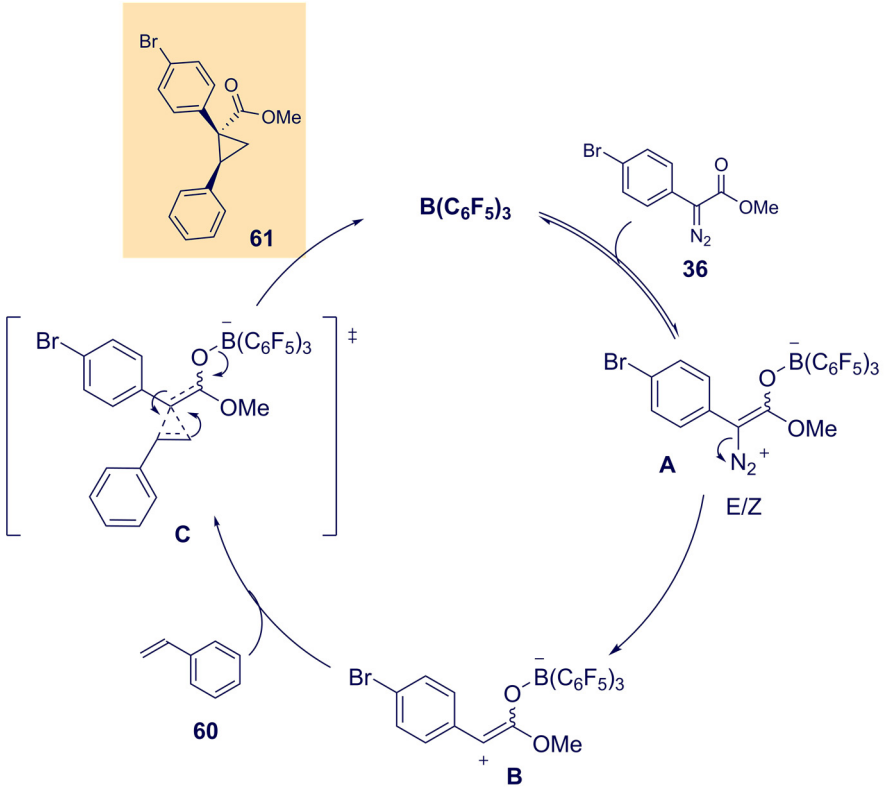
Scheme 20. Metal-free alkenylation reactions of aryl esters with α-diazoesters.

Methods for cyclopropanes' synthesis are crucial for many research areas such as drug discovery, chemical biology, and total synthesis. Hill's research group reported an intriguing strategy for the cyclopropanation of unactivated alkenes using aryldiazoacetates by exploiting the strong sterically encumbered Lewis acid (BCF) as catalyst (Scheme 21). The cyclopropane products are synthesised via a Lewis acid-activated carbene using 10 mol% of the catalyst under mild conditions [46].



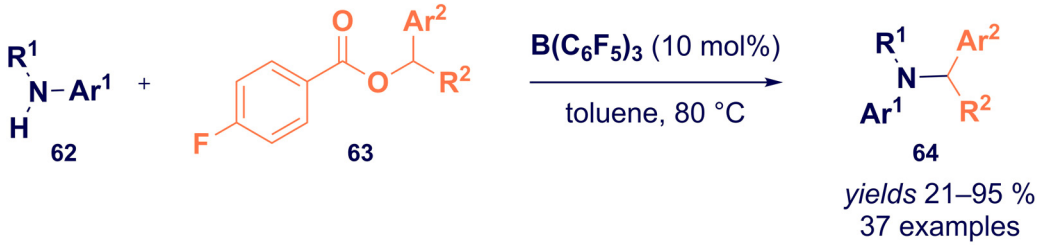
Scheme 21. Cyclopropanation of unactivated alkenes using aryldiazoacetates by BCF catalysis.

Scheme 22 shows the catalytic cycle. First BCF coordinates reversibly to the ester on diazo compound **36** because of its oxophilic nature. Then the formation of the alkene diazonium ion species **A**, as a mixture of E- and Z-isomers, occurs. At this point, the Lewis acid-activated carbene intermediate **B** is formed by losing N_2. This electrophilic intermediate then undergoes a concerted [2 + 1] cycloaddition reaction with the vinyl group on styrene derivative **C**, forming the desired products **61** and regenerating the Lewis acid catalyst. The high diastereoselectivity of the cycloaddition is probably given by the steric hindrance of the styrene aryl group and the bulky tris(pentafluorophenyl)borane.



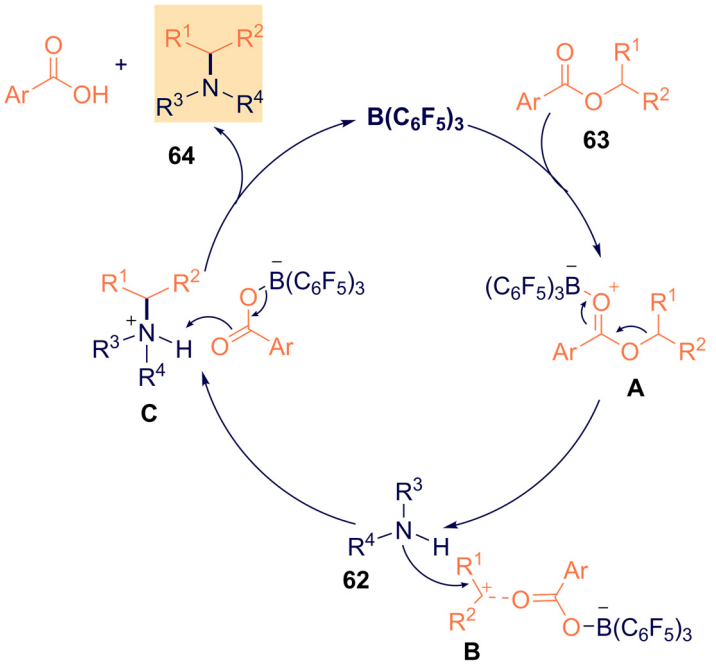
Scheme 22. Mechanism for the BCF-catalyzed cyclopropanation.

One more noteworthy strategy is reported by Melen et al.; they set up a mild and facile BCF-catalysed approach to construct new C–N bonds; thanks to this strategy N-alkylation reactions of a wide variety of amine **62** substrates with aryl esters **63** is performed. This reaction protocol yields a wide range of N-alkylated products **64** in good to excellent yields. The construction of a C–N bond at the propargylic position has also been demonstrated to provides access to this synthetically useful propargyl amines moiety. On the other hand, a trend-reversal is seen in unsubstituted 1H-indoles and 1H-pyrroles at the C3/C2 positions afforded exclusively C–C coupled products (Scheme 23) [47].



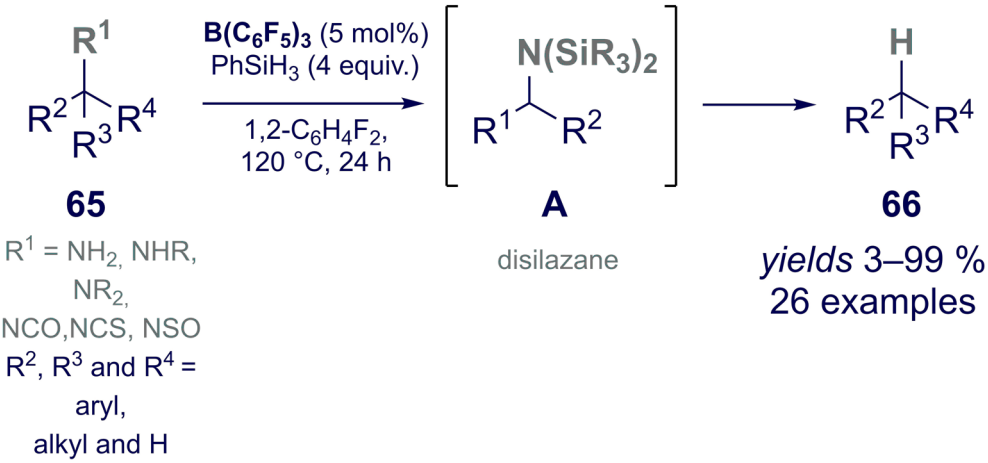
Scheme 23. N-alkylation reactions of amine derivatives **62** with aryl esters **63** using BCF as catalyst.

Extensive DFT calculations were performed by Melen et al. to investigate the reaction mechanism (Scheme 24). At first the coordination of the borane to the ester occurs (intermediate **A**). This coordination causes the elongation of C–O bond at its subsequent cleavage, generating an electrophilic carbenium ion **B**. Then the nucleophilic attack of a variety of amines **62** to the electrophilic carbenium ion **B** formed in situ occurs. Finally, the intermediate **C** undergoes to the deprotonation reaction and the desired N-C coupled product **64** and benzoic acid (byproduct) were released.



Scheme 24. Mechanism for the BCF-catalyzed N-alkylation.

The strong boron Lewis acid BCF is known to catalyze the dehydrogenative coupling of certain amines and hydrosilanes at elevated temperatures. At higher temperature, the dehydrogenation pathway competes with cleavage of the C–N bond and the defunctionalisation occurs. This feature of BCF can be turned into a useful tool for the transition-metal-free reductive deamination of a broad range of amines **65** (26 examples) as well as heterocumulenes, isocyanates and isothiocyanates (Scheme 25) [48]. The desired defunctionalised products **66** were obtained in moderate to excellent yields, apart from a couple of examples.

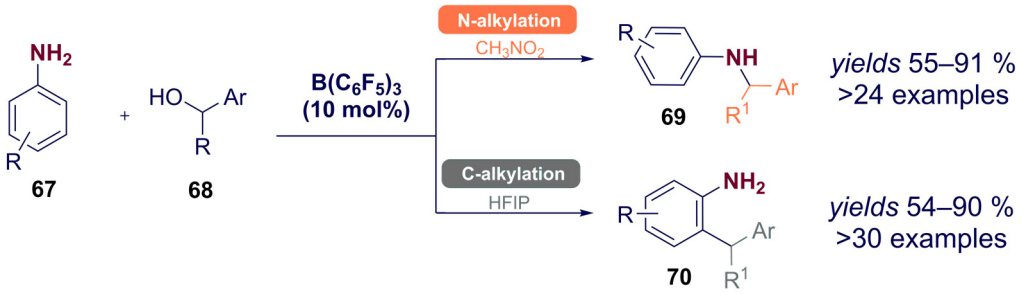


Scheme 25. Transition-metal-free catalytic reductive N–C bond cleavage.

The authors reported a series of mechanistic experiments and they concluded that the dehydrogenative Si-N coupling of the bis-silylammonium borohydride intermediate is in competition with its dissociation into the corresponding benzylic carbocation and disilazane **A** because of the high temperature. The carbocation formed in situ is then captured by the borohydride to afford the desired defunctionalised product.

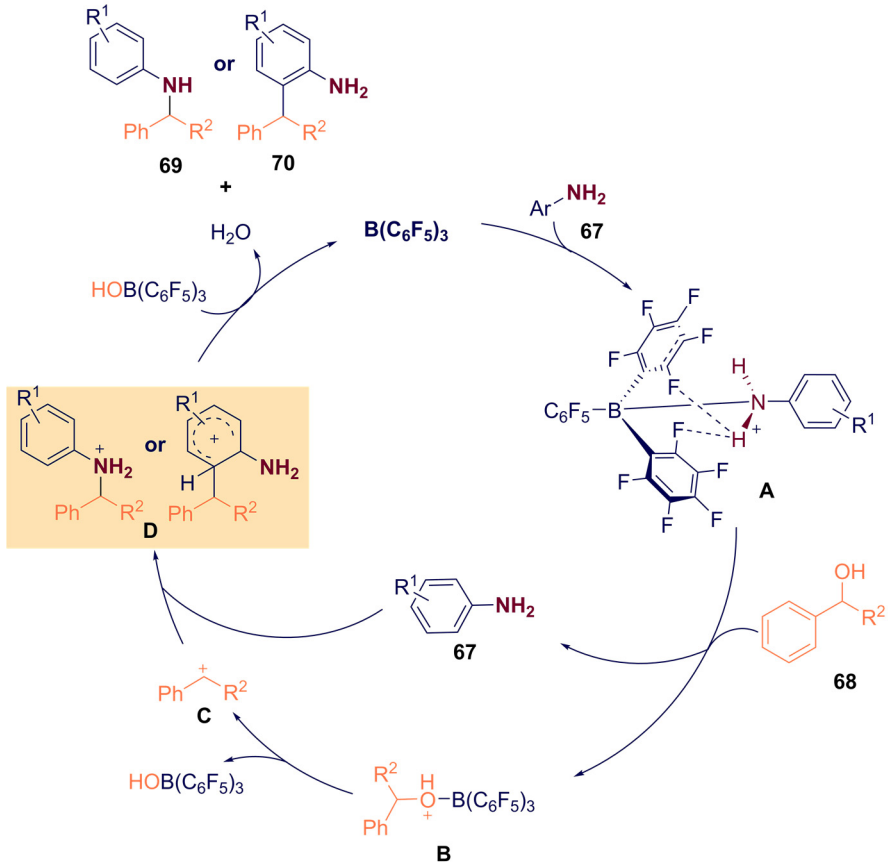
In 2019 an unprecedented protocol for the efficient and highly chemoselective alkylation of unprotected arylamines **67** coupled with alcohols **68** mediated by BCF was demonstrated by Chan's research group (Scheme 26). N-alkylated products and ortho C-alkylated

products were obtained using different solvents in good chemoselectivities and yields. The borane underwent alcohol/arylamine exchange to ensure the catalytic activity [49].



Scheme 26. Chemoselective alkylation of arylamines using alcohols mediated by BCF.

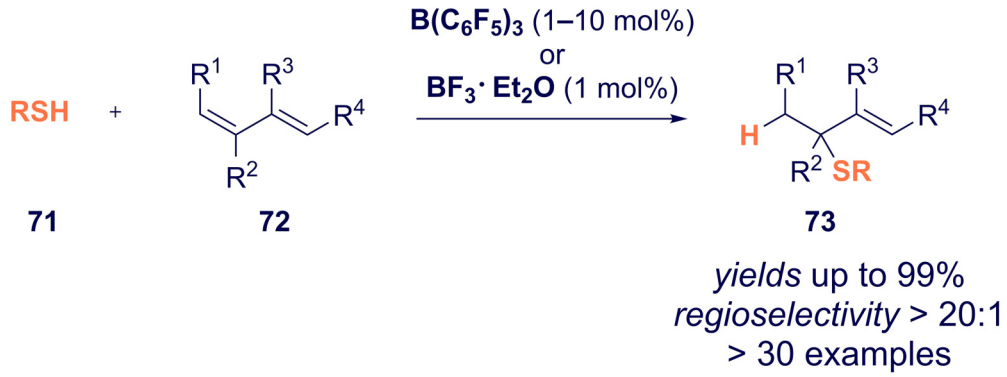
Both mechanistic studies and DFT calculations proposed that the reaction pathway proceeds through four-steps as shown in the Scheme 27: at first the alcohol/amine exchange generates catalyst-alcohol complex intermediate **B**; then, the dissociation of the intermediate formed in situ occurs and the carbocationic specie **C** is formed. At this point the nucleophilic attack of the carbocation **C** by the arylamine **67** generates the N-/C-alkylation intermediates and finally after the protolysis of the σ-complex intermediates **D** the desired N-/C-alkylated products **69** or **70** are formed and the catalyst is released.



Scheme 27. Mechanism for the BCF-catalyzed N/C-alkylation of arylamines.

A novel metal-free hydrothiolation of 1,3-dienes for preparing secondary and tertiary allylic sulfides was recently reported by Chatterjee et al. (Scheme 28). The boron Lewis acids BCF and $BF_3{\cdot}Et_2O$ are shown to catalyze the regioselective hydrothiolation of numerous terminal 1-aryl-1,3-dienes **72**. In the case of internal 1,3-dienes, BCF is a better catalyst than $BF_3{\cdot}Et_2O$ by a large margin. This methodology has the advantage of being performed

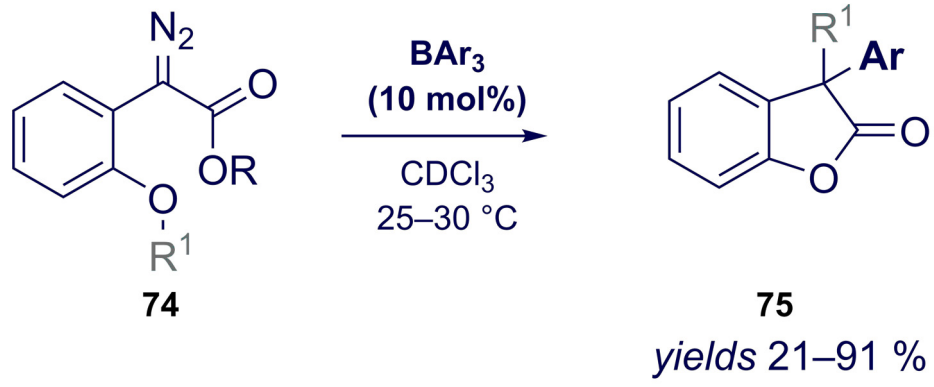
under mild reaction conditions and low catalyst loading. Furthermore, this protocol is rate-limited by the 1-aryl-directed protonation of 1,3-dienes with thiol-boron Lewis acid complexes, followed by sulfide anion transfer to the resultant allyl cations [50].



Scheme 28. Novel metal-free hydrothiolation of 1,3-dienes mediated by BCF.

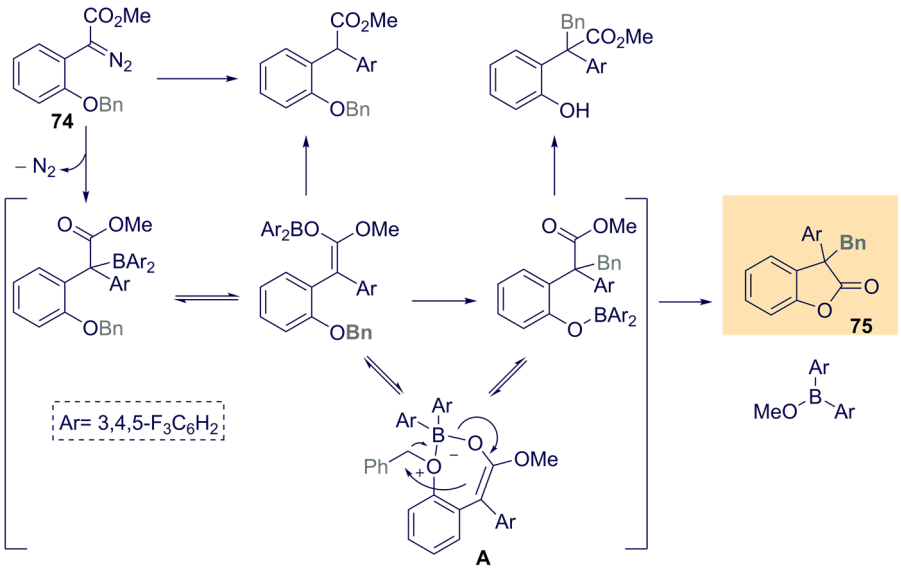
To better understand the mechanism of the protocol under investigation, the authors performed both experimental and theoretical studies. The reaction proceeds with the protonation of the 1,3-diene **72** and it is finalized by the C–S coupling driven by the Lewis adduct formation between the acidic borane and thiol 71. In fact, it is shown that thiophenol and BCF may easilier form a weak B···S adduct instead of the 1,3-diene and BCF adduct, which is much less favorable.

In 2017 Melen's research group fine-tuned a novel metal-free synthesis of 3,3-disubstituted benzofuran-2-(3H)-ones **75**, by reacting α-aryl-α-diazoacetates **74** with triarylboranes (Scheme 29). Initially, triarylboranes were successfully investigated in α-arylations of α-diazoacetates **74**; however, in the presence of a heteroatom at the ortho position, the boron enolate intermediate **A** undergoes an intramolecular rearrangement to form a quaternary center. Then this intermediate cyclises to afford valuable 3,3-disubstituted benzofuranones [51].



Scheme 29. BCF catalysed synthesis of 3,3-disubstituted benzofuran-2-(3H)-ones.

Mechanistically, at first the 1,2-aryl shift from the borane to the diazocompound **74** with loss of dinitrogen and formation in situ of the boron enolate intermediate **A** (Scheme 30). This intermediate fully converts into the corresponding ester within 1 h. Finally, the desired lactone **75** and the diarylboronic ether as side product within 24 h.

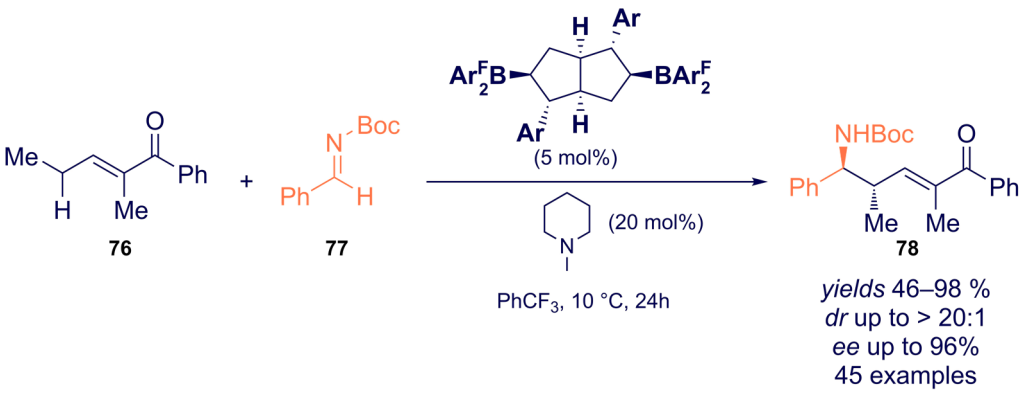


Scheme 30. Mechanistic investigation for the BCF-catalyzed synthesis of 3,3-disubstituted benzofuran-2-(3H)-ones **75**.

3.2. Asymmetric Boron-Based Catalysis

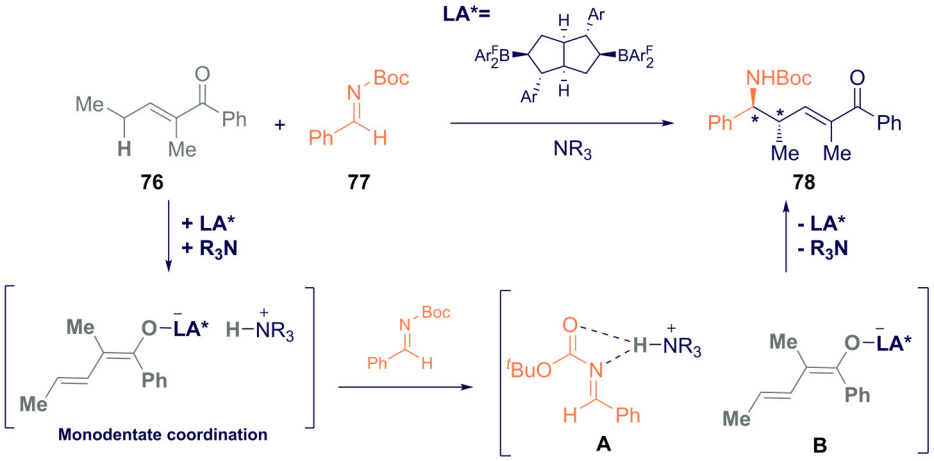
Boron Lewis acids are also promising as chiral catalysts; however, this field remains largely unexplored due to some critical challenges. The main hurdle is the moisture-sensitivity of these catalysts, which makes boron Lewis acid components difficult to prepare and handle. Therefore, the development of convenient methods for the preparation of chiral boron Lewis acids is an hot topic.

Wang's research group reported a ground-breaking strategy to perform the asymmetric vinylogous Mannich reaction of acyclic α, β-unsaturated ketones **76** providing an efficient approach to synthesise enantiopure amino-functionalised derivatives **78**. These products are appealing building blocks for the synthesis of pharmaceutical and natural compounds. Most often, the interaction between drugs and their natural receptors is enantioselective, therefore it is crucial that these synthetic processes yield only one enantiomer. By combining the chiral bicyclic bisborane catalysts with a tertiary amine, the asymmetric vinylogous Mannich reactions of α,β-unsaturated ketones **76** with Boc-protected imines **77** was successfully accomplished with excellent regio-, diastereo-, and enantioselectivities (Scheme 31). Thanks to this efficient methodology, the desired products were obtained in good to excellent yields (up to 98%), high diasteroselectivity (up to >20:1) and very high enantiomeric excess (up to 96%) [52].



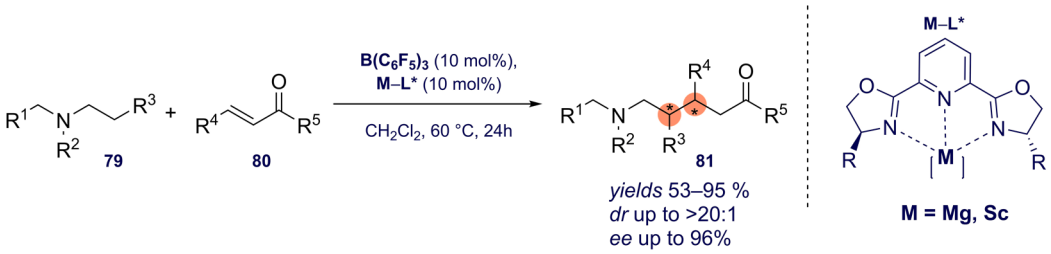
Scheme 31. Asymmetric vinylogous Mannich reaction of acyclic α, β-unsaturated ketones **76** via asymmetric boron-based catalysis.

The Lewis acid catalyst and the base cooperatively deprotonated the substrate to obtain synergistically two valuable intermediates: a borane-ligated vinylogous dienolate **B** and an ammonium cation **A**, which then acts as a Brønsted acid to activate the imine while the borane controlled the selectivity of the Mannich reaction (Scheme 32). Theoretically, coordination of the carbonyl oxygen with a strong Lewis acid catalyst would facilitate deprotonation by inductively increasing the acidity of the γ proton and thus favor enolization of the substrate. In fact, the strong Lewis acidity and steric hindrance of the bisborane catalysts were critical to induce the high selectivities and yields.



Scheme 32. Mechanistic investigation for the asymmetric vinylogous Mannich reaction.

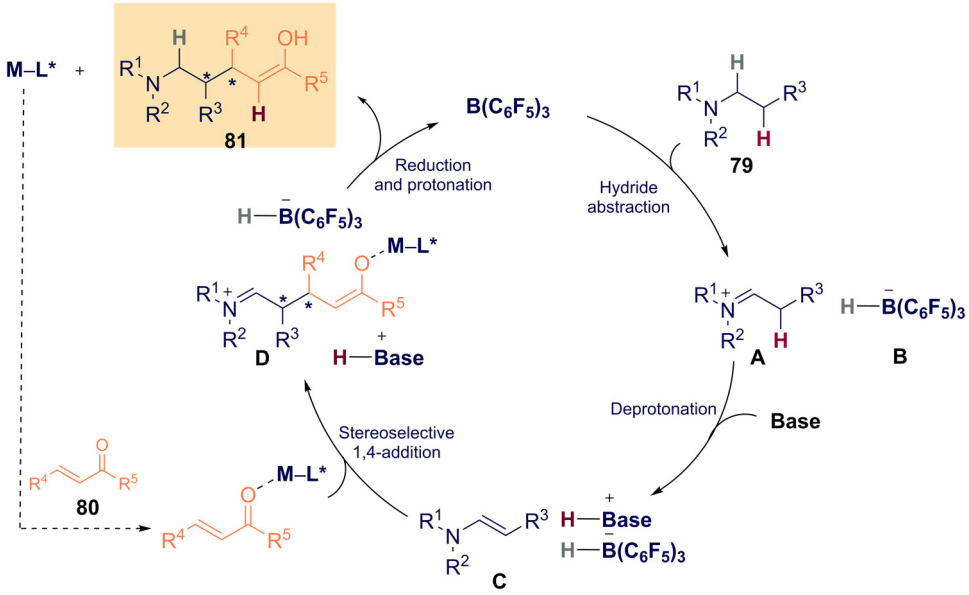
Another elegantly designed approach has been recently developed to obtain the β-C(sp^3)−H functionalization of N-alkylamines **79** reacting with α,β-unsaturated compounds **80**. This cutting-edge methodology allows the enantioselective late-stage β-C−H functionalization of bioactive amines which revealed itself to be a powerful strategy to access key building blocks of N-based natural products and drugs [53]. Wasa et al. fine-tuned a synthetic approach which exploits the cooperation of two different catalysts which in appearance could act competitively: a Lewis acid, BCF, and a chiral Mg- or Sc-based complex. Surprisingly, this strategy was successful, and by carefully choosing the reaction conditions, a spectrum of δ-amino carbonyl compounds **81** was synthesised by enantioselective reaction of a N-alkylamine-derived enamine and an electrophile (i.e., the α,β-unsaturated compound) simultaneously activated by the chiral Lewis acid (Scheme 33). The protocol designed and performed proves itself to be efficient (yields up to 95%), highly disteroselective (up to >20:1) and highly enantioselective (*ee* up to 96%).



Scheme 33. Enantioselective β-C−H functionalization of N-alkylamines **79**.

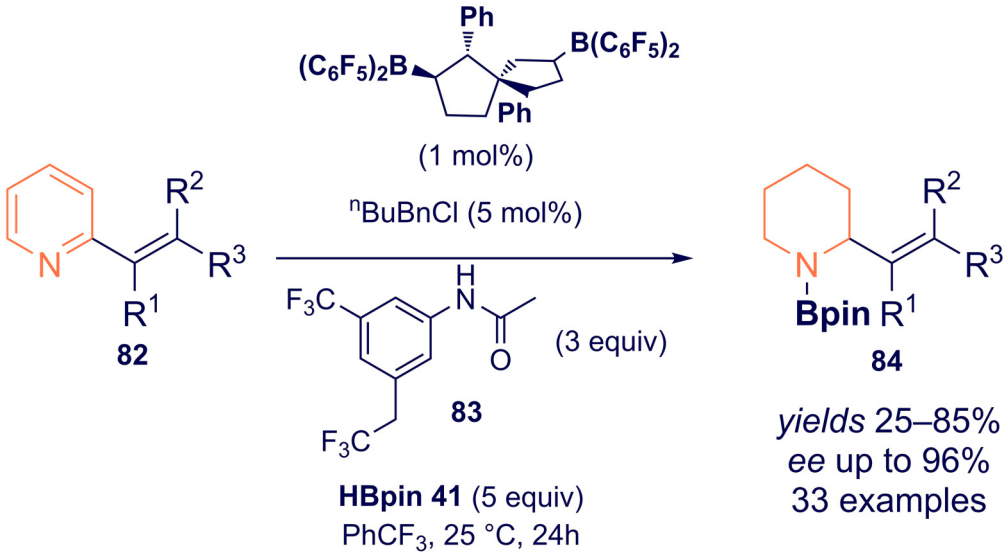
The authors propose that BCF could abstract a hydride from the amine, leading to the formation of a borohydride **B** and an iminium ion intermediate **A**. A Brønsted base catalyst subsequently deprotonates the iminium ion to give the corresponding enamine **C**. The enamine **C** and α,β-unsaturated compound **80**, activated by the chiral Lewis acid co-catalyst, undergo enantio- and diastereo-selective C−C coupling reaction, obtaining a

zwitterionic intermediate **D**. Then, the protonation and reduction of the resulting intermediate formed in situ follows to give the desired β-alkylation product **81** (Scheme 34).



Scheme 34. Mechanistic perspective for the enantioselective β-C−H functionalization of N-alkylamines **79**.

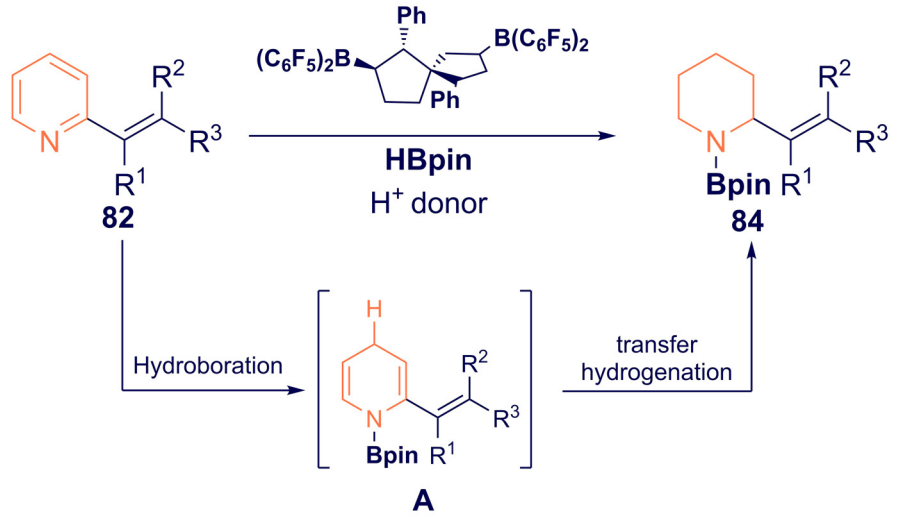
One more key example was reported by Wang's research group: a highly chemoselective and enantioselective reduction of 2-vinyl-substituted pyridines **82** was achieved by exploiting chiral spiro-bicyclic bisboranes as catalysts, and HBpin **41** and an acidic amide as reducing reagents **83** (Scheme 35). This protocol is not only the first example of a metal-free borane-catalysed enantioselective pyridine reduction, but also an uncommon approach to enantioselectively reduce unprotected pyridines. The excellent functional group tolerance of this efficient methodology is one of the major strengths of this protocol; in addition, the low catalyst loading and the mild reaction conditions (ambient temperature and no use of compressed hydrogen gas) make it attractive for industrial applications [54].



Scheme 35. Enantioselective reduction of 2-vinyl-substituted pyridines.

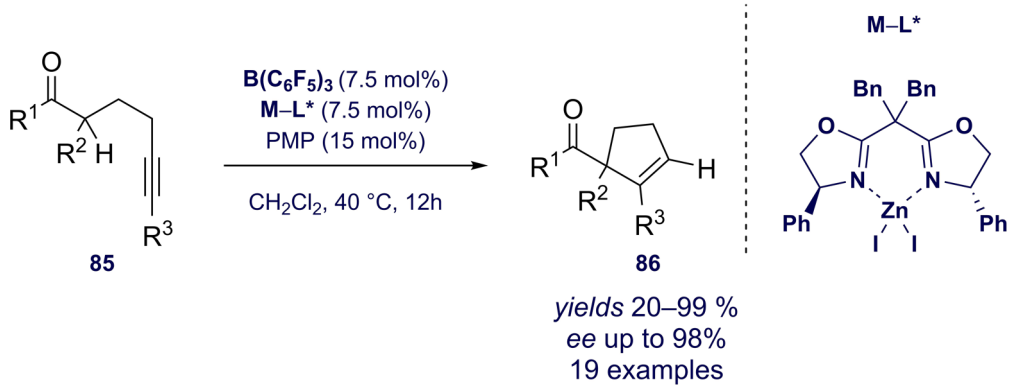
The cooperative activation of HBpin **41** is presumably obtained by the borane catalyst and the pyridine to generate the borenium cation and the borohydride anion. Then, the

hydride transfer from the borohydride anion to the 4-position of the pyridine ring occurs and the Bpin-protected dihydropyridine intermediate **A** is formed. The reaction of HBpin, the proton donor and the borane catalyst provide the borohydride anion and the ammonium ion, which act as reducing reagents for transfer hydrogenation of the dihydropyridine intermediate (Scheme 36).



Scheme 36. Proposed mechanism for the enantioselective reduction of 2-vinyl-substituted pyridines **82**.

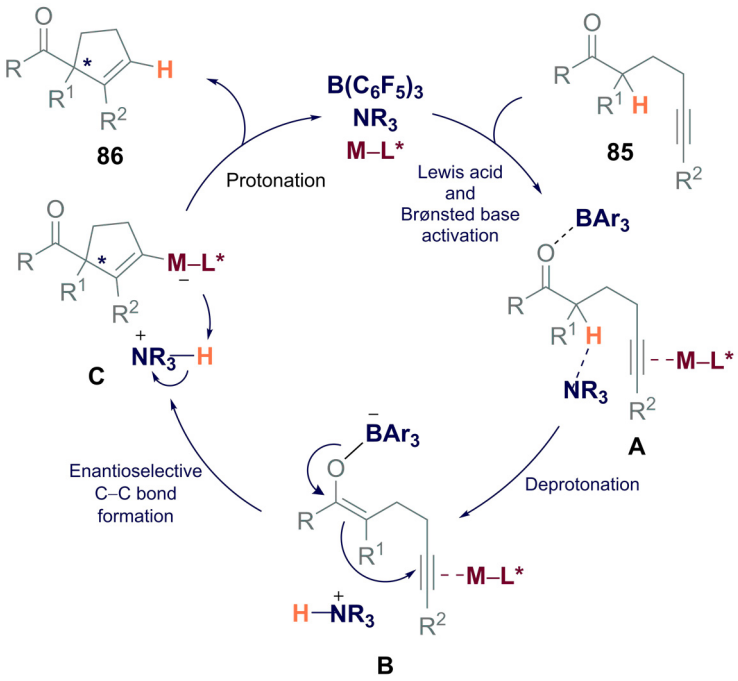
An efficient and highly enantioselective Conia-ene-type reaction has been developed by Wasa and coworkers as the Scheme 37 shows [55]. This exploits the cooperative action of a three-component catalyst system, consisting of a pair of Lewis acids and a Brønsted basic amine (i.e., BCF, a BOX–ZnI_2 complex and an N-alkylamine respectively). The cornerstone of this pioneering work lies in the judicious tuning of different Lewis acids which possess complementary features. Thanks to this *escamotage* ketones with poorly acidic α-C–H bonds can be converted in situ to the corresponding enolates through BCF and amine which work in concert. Subsequently the enantioselective cyclization occurs by a BOX–ZnI_2-activated alkyne **85** and the desired Conia-ene-type reaction products **86** are obtained with excellent yields (up to 99%) and enantioselectivities (up to 98%).



Scheme 37. Enantioselective Conia-ene-type reaction mediated by a three-component catalyst system: BCF, N-alkylamine (PMP) and a BOX–ZnI_2 complex.

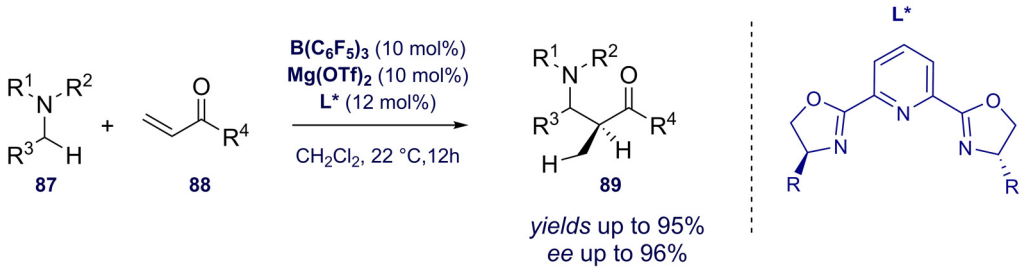
The authors propose that first N-alkylamine could deprotonate BCF-activated ketone (intermediate **A**), generating an enolate **B** and an ammonium ion. In the meantime, a chiral Lewis acid cocatalyst (M–L*) would activate the alkyne moiety. Then, the enantiodetermining 5-endo-dig cyclisation of the enolate and the alkyne occurs (intermediate **C**).

Subsequent protonation of C–ML* bond by the ammonium ion would afford the desired cyclopentenyl product 86 (Scheme 38).



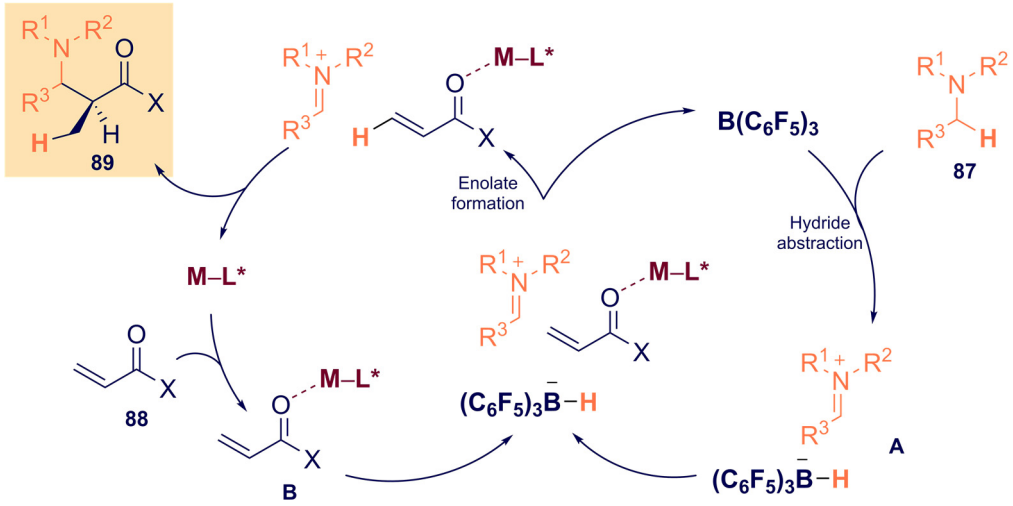
Scheme 38. Mechanism for the enantioselective Conia-ene-type reaction.

In 2018, Wasa et al. developed a methodology to synthetise valuable enantiomerically enriched α-substituted amines (Scheme 39) [56]. Hence, a strategy for the enantioselective coupling of N-alkylamines **87** and α,β-unsaturated compounds **88** was designed and successfully performed, which allowed them to obtain a wide range of α-amino carbonyl compounds **89** with excellent yields (up to 95%) and enantioselectivity (up to 96%). At the basis of this work there is the employment of the cooperative action ofBCF, the Lewis acids counterpart, and a chiral Mg–PyBOX complex, which acts as a base, to induce the enantioselectivity. This approach outperforms traditional methodologies which require oxidative conditions and precious transition metal catalysts.



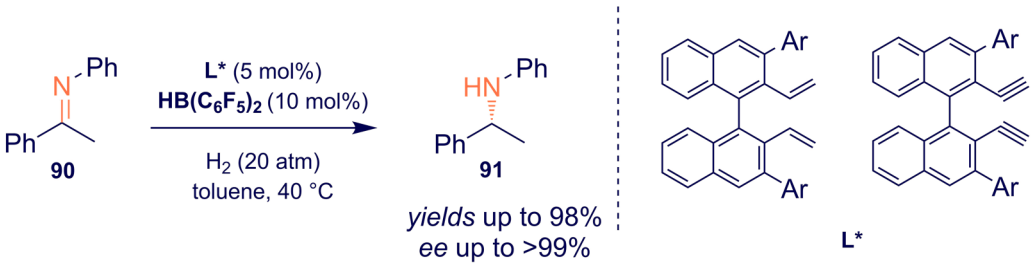
Scheme 39. Synthesis of chiral α-substituted amines **89** via cooperative catalysis of BCF and chiral Mg–PyBOX complex.

A possible mechanism proposed by the authors involves the enantio- and diastereoselective C–C coupling between iminium ion **A** and chiral enolate **B**, both generated in situ by cooperative functions of a chiral (Mg–PyBOX complex) and an achiral (BCF) Lewis acid catalyst as Scheme 40 shows.



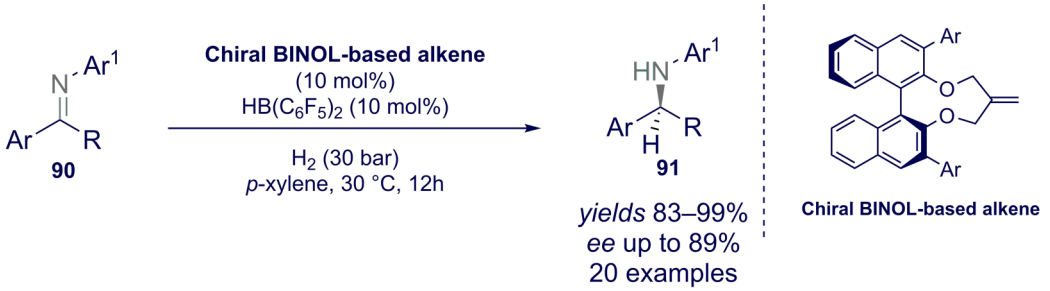
Scheme 40. Mechanism for the synthesis of chiral α-substituted amines.

Du and coworkers proposed a novel cutting-edge strategy for generating chiral boranes in situ via hydroboration of chiral terminal dienes or diynes, that can act as ligands, with Piers' borane without further purification. Thanks to this approach, asymmetric metal-free hydrogenations and hydrosilylations become more rapid and operationally simple. With chiral diene-derived boron Lewis acids as catalysts, a broad range of unsaturated compounds, such as imines, silyl enol ethers, 2,3-disubstituted quinoxalines, and polysubstituted quinolines, show itself to be suitable substrates for asymmetric metal-free hydrogenations, giving the corresponding products in excellent yields (up to 98%) and high enantioselectivities (up to >99%) (Scheme 41) [57]. The mechanism for the reduction of imines **90** to amines **91** is well known by previous literature reports but, in this specific approach, the chiral alkenylboranes were designed ad hoc to enhance the rigidity of the framework essential to maximise the enantio-induction.



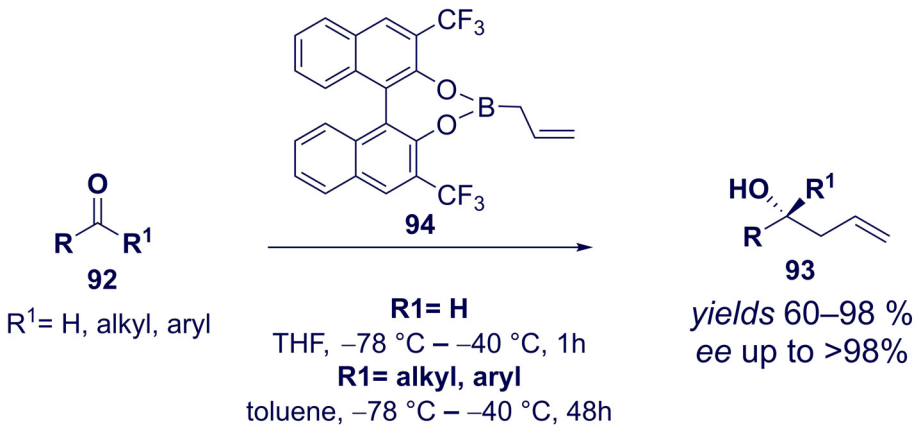
Scheme 41. An example of chiral diene-derived boron Lewis acids employed as catalysts.

Building on this novel intriguing approach, with the aim of developing easily accessible chiral Lewis acids for asymmetric hydrogenation of imines, Du's research group created a variety of binaphthyl-based chiral alkenes, prepared in one step from the corresponding diols. Using in situ generated chiral boron Lewis acids through hydroboration of chiral alkenes with Piers' borane, metal-free asymmetric hydrogenations of imines **90** was performed to successfully obtaining the reduced products **91** in high yields (up to 99%) and elegantly controlled enantioselection (*ee* up to 89%) (Scheme 42) [58].



Scheme 42. Asymmetric hydrogenations of imines.

A similar asymmetric boron-based catalyst was employed by Chong's research group; allylboronates **94** derived from 3,3′-disubstituted 2,2′-binaphthols allowed the asymmetric allylation of aldehydes and ketones **92** (Scheme 43). The bis(trifluoromethyl) derivative proved to be particularly efficient in terms of reactivity (yields up to 98%), selectivity (*ee* up to >98%), and robustness [59]. The allylations using R-BINOLs gave R alcohols as major enantiomer because of the transition state formed, which affected by the electronic and steric effects of the -CF_3 substituents.



Scheme 43. Asymmetric allylation of aldehydes and ketones.

4. Conclusions

The use of boranes in catalysis has recently seen an increasing interest; besides exploring new reactivities, boron catalysis allows to perform known reactions in milder conditions. The difficulty in synthesising and handling boron catalysts caused this research field to remain dormant for long time. This review focused on the recent developments to provide an overview of the field and a perspective of where it may be heading. In fact, given the traction and the importance in synthesis that it is currently gaining, this relatively new field of catalysis holds high potential and will continue to greatly contribute to synthetic chemistry, both in academia and industry.

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