
**FINAL RESEARCH PAPER**

# THE USE OF ORGANOTRIFLUOROBORATES IN THE INTRAMOLECULAR BORON-MEDIATED CONJUGATE ADDITION TO IMINO-DERIVATVES

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## Abstract

The use of organotrifluoroborates provide an organocatalytic approach to form new carbon-carbon bonds through boron-mediated transfers. With a particular focus on intramolecular conjugate this work focuses on the addition to imino-derivatives. During the course of this study, variety of starting imines were successfully synthesized using a simple and efficient method. This work focuses on the examination of the transfer of both an alkyl (butyl) and an allyl group under various reaction conditions. Although successful butyl-transfer could not be cleanly achieved, valuable data on the behavior of the participating reagents was collected in hopes of moving that part of the study forward. However, a successful allyl-transfer was achieved, and with careful and extensive NMR analysis the product of the reaction could be identified. This work brings new methodology to the field that is free from metallic catalysis. It opens up the possibility for more environmentally friendly approaches to carbon-carbon bond formation and sets the stage for future research in the field.



Keywords: organotrifluoroborates, boron-mediated transfers, conjugate addition to imino-derivatives, alkyl and allyl transfer

# Table of Contents

# List of Figures

# List of Schemes

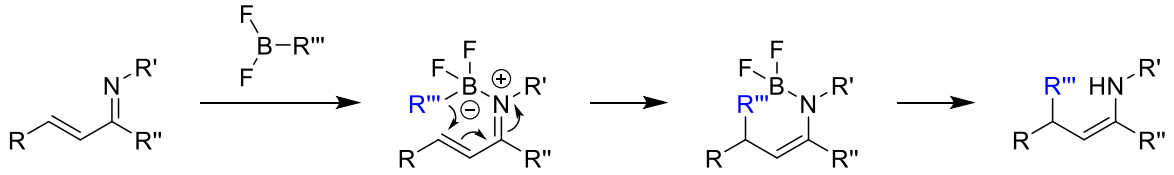
# List of Tables

## List of Abbreviations

| | |
|---|---|
| GC | Gas Chromatography |
| MS | Mass Spectroscopy |
| NMR | Nuclear Magnetic Resonance |
| TLC | Thin-Layer Chromatography |
| LG | Leaving Group |
| $CDCl_3$ | Deuterated Chloroform |
| $CD_3CN$ | Deuterated Acetonitrile |

# 1 Introduction

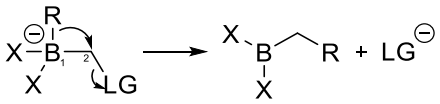
Carbon-carbon bonds make up life as we know it as they are the key building block in the structure of every organic molecule. Therefore, the ability to make such bonds is of utmost importance to natural product synthesis. In organic chemistry, carbon-carbon bonds are used to build molecules with a variety of properties and functions. Additionally, compounds that contain a nitrogen atom can be found in almost every biologically important molecule and pharmaceutical.[1] A general method that forms a new carbon-carbon bond in near proximity to a nitrogen atom would be an important addition to organic reaction methodology and pharmaceutical development. The addition of carbon-based nucleophiles to electrophilic imine counterparts is not as common or efficient as it can and should be, especially when looking at similar chemistry with its carbonyl cousin. To tackle this problem, alterations have been made in the past to increase electrophilicity or to stabilize the impending anionic character on the imine N.[2,3] Similar chemistry was done by May et al.[4] In his work the use of a catalyst and additive has been employed. However, the organocatalytic approach of this work to carbon-carbon bond formation via a boron-mediated transfer brings new methodology to the field. Making the use of organotrifluoroborates as reaction partners this method is free from metallic catalysis and separate preparation of a third-party catalyst. This chemistry would allow to functionalize the β-position of an α,β-unsaturated imine with variable constitution and with the specific control of substitution of the resulting enamine.




Scheme 1: General Scheme of the Addition to Imines

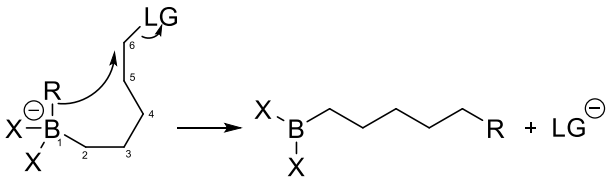
## 1.1 Boron-mediated transfers

Boron-mediated transfers are an important tool in organic chemistry and have a wide range of application in the synthesis and modification of organic molecules. As they offer the possibility to achieve new carbon-carbon bonds they are in the focus of this work. Boron-mediated transfers can be defined as nucleophilic transfers of a carbon containing moiety from boron to a nearby electrophilic carbon center. If the carbon center is adjacent to the boron, it will result in a boron-mediated 1,2 transfer as the numbering starts at the boron and ends at the carbon center where the new bond will be formed (Scheme 2).




Scheme 2: Boron-mediated 1,2 transfer

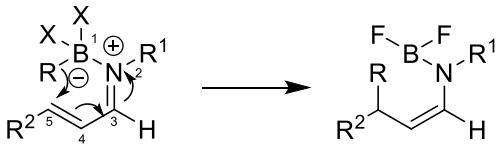
A new carbon-carbon bond is formed during this process. This characterization can be continued in the same manner all the way through to boron-mediated 1,6 transfers (Scheme 3).[5]




Scheme 3: Boron-mediated 1,6 transfer

Due to organoboron chemistry's growing impact on general methodology, researching this topic can provide a wealth of information and potential value. Therefore, investigating this area is a worthwhile endeavor.

This work only focuses on a small part of this topic due to its wide scope. Here, the focus lies on a boron-mediated 1,5 transfer via conjugate addition to the β-position of an imine (Scheme 4).

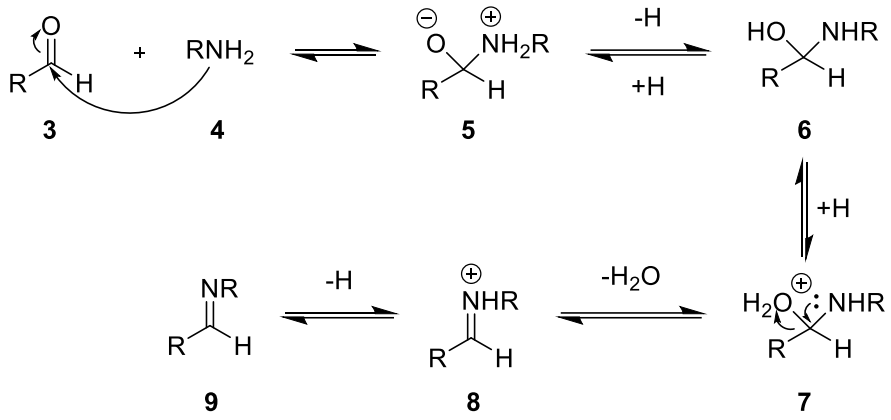



**1** **2**

Scheme 4: Aimed for boron-mediated 1,5 transfer

## 1.2 Synthesis of imines

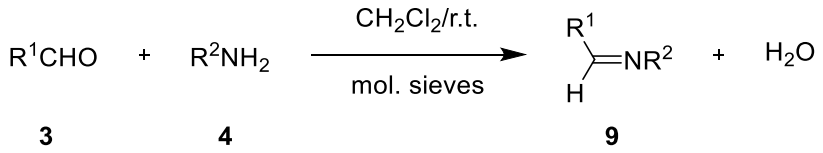
Imines are prepared from the respective aldehyde or ketone and primary amine. As an amine is added and water is removed during this process, this is a nucleophilic addition-elimination reaction.




Scheme 5: Mechanism of imine formation

Two different approaches to the starting imines were pursued in this work.

The first approach was an in this laboratory previously well-established route, namely the one of Mangeney et. al (Scheme 6).[6]




Scheme 6: Imine formation (Mangeney)

Methylene chloride was used as a solvent and molecular sieves were added to remove the water formed in the reaction.

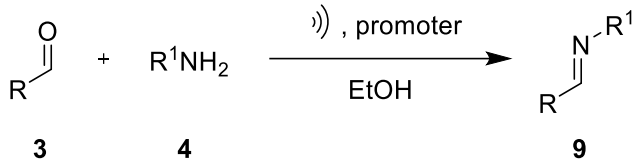
As the purification with column chromatography ended up in hydrolyzing the product another route was taken in the course of the laboratory work. This method is based on the work of Stefani et. al.

Several methods have already been developed by Stefani et. al. for the implementation of ultrasound irradiation in the synthesis of various organic compounds, as aryl acetylenes and heterocycles.[7–9] Furthermore, he also explored the use of ultrasound for more efficient Suzuki-Miyaura reactions.[10]

The application of ultrasound in chemistry is often referred to as sonochemistry. Making use of ultrasound often leads to more efficient reactions. Those effects are attributed to cavitation. Gaseous and vaporous cavities are formed within a liquid subjected to ultrasound irradiation. This process generates higher temperatures and pressure inside the bubbles, resulting in turbulent flow and increased mass transfer.[10]

Using ultrasound in these reactions offers a range of advantages over conventional methods. Firstly, the process is relatively mild and simple. These attributes help to minimize the environmental impact of the production process and increase operational safety. Additionally, it is a highly efficient process with an easy work-up, which leads to a shorter reaction time in comparison to previous used methods. On top of that, the process delivers good yields. Overall, this implementation of ultrasound is a practical and attractive option for the synthesis of different important organic molecules, offering a more streamlined and sustainable approach to the production of the respective product.[7–10]

With his past work looking so promising, Stefani et. al. also looked on the ultrasound-assisted production of imines through the reaction of the respective aldehydes and primary amines. Testing different promoters, such as alumina, silica, resins and celite, using five equivalents of silica seemed to be the best way to go (Scheme 7).[1]




Scheme 7: Imine formation (Stefani)

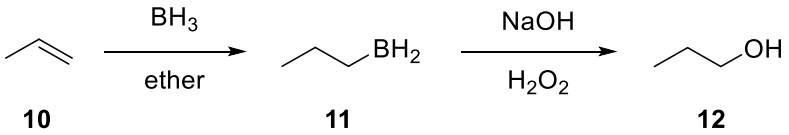
This process leads to quite high yields and clean products, even in large scale synthesis. As many of the already described methods in literature are very complex and take long times, this new method provides a more efficient approach to imine production.

As this mild and convenient method delivers very clean products in a very short time using common laboratory techniques this route was taken for future synthesis of starting imines.

## 1.3 Organoboron Chemistry

### 1.3.1 Hydroboration-Oxidation

The use of boron in organic synthesis is inevitable due to the possibilities that it brings to the field. One of the most common examples where boron is used is hydroboration, which is often followed by an oxidation reaction (Scheme 8). Within these two successive reactions an alkene is converted to an anti-Markovnikov alcohol.



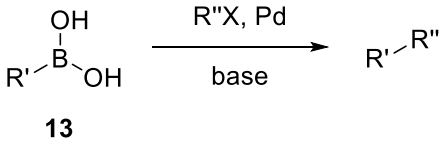

Scheme 8: Hydroboration/Oxidation

This reaction can be found in every Organic Chemistry textbook as one of the first examples when talking about reactions of alkenes and alkynes. It is a widespread and well-known reaction. When looking at it from a boron point of view the second step could be seen as a boron-mediated 1,2 transfer in which a carbon-oxygen bond is formed.

Hydroboration plays a big part in organic synthesis and shows a boron-mediated transfer, but it lacks the formation of a carbon-carbon bond.[5]

### 1.3.2 Suzuki reaction

Boron also finds use in the highly popular Suzuki reactions (Scheme 9).[5] The Suzuki reaction does provide a powerful way to make a new carbon-carbon bond, but it does not require the direct involvement of boron for that bond formation.



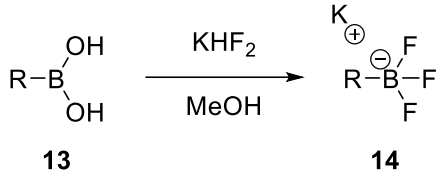

Scheme 9: Suzuki reaction

Further, for that reaction to work, a palladium catalyst is needed. The aim of this work is to evaluate a method that does not make use of metallic catalysis.

Both reactions show the importance of boron in organic synthesis. Additionally, both show certain characteristics of the focus of this work and the targeted carbon-carbon bond formation via boron mediated transfer. To combine both elements, organotrifluoroborates were utilized for the direct involvement of the boron and further creation of the new carbon-carbon bond.

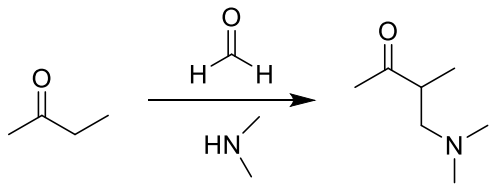
### 1.3.3 Trifluoroborates

Organotrifluoroborates are mild and easily handled reaction partners.[11] Their ease of use and bench-top stability make them very attractive to organic chemists.[4,12] Additionally the simple preparation method from respective boronic acids provide a short way to trifluoroborate starting materials (Scheme 10).[13]

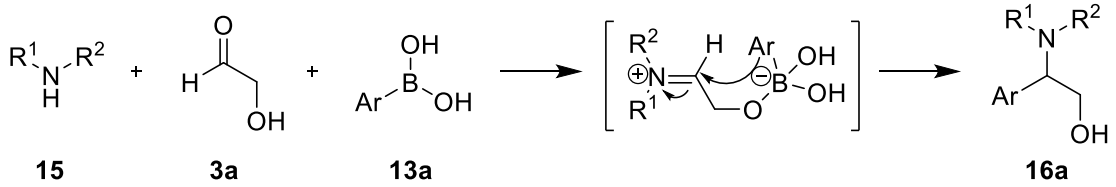



Scheme 10: Synthesis of trifluoroborates

The use of organotrifluoroborates is already established in various reactions and the interest in them as reaction partners only continues to grow. For the purpose of providing one example where they can be found, the acid promoted Petasis reaction is being considered.[11] The Petasis reaction is a three component Mannich-type coupling reaction producing functionalized amines from boronic acid, aldehyde and amine starting materials (Scheme 11, Scheme 12).

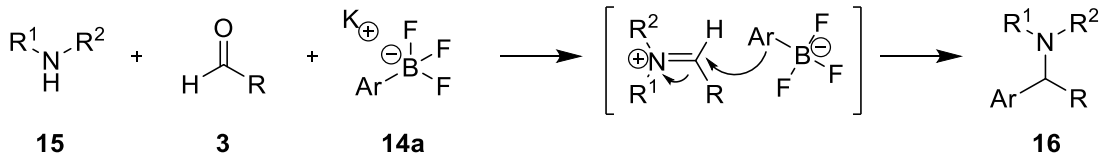



Scheme 11: Mannich Reaction




Scheme 12: Petasis Reaction

But here the limitation is the need of a heteroatom on the iminium-ion for the intramolecular addition to happen. To overcome this limitation Carrera is using trifluoroborates instead of boronic acids and makes an extension to the standard Petasis reaction (Scheme 13).

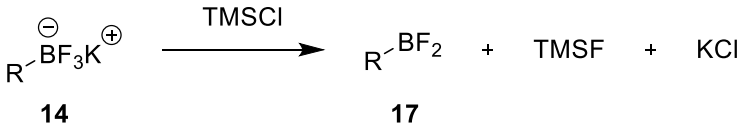



Scheme 13: Petasis reaction with organotrifluoroborates

In his work he shows the scope of this method by adding vinyl, hetero- and aromatic trifluoroborates to different carbamate protected electrophiles, such as imines and enamines.[11]

For the reaction examined in this study, the in-situ preparation of Lewis acidic organo-difluoroboranes is necessary for the trifluoroborates to react with the imine counterpart. During the course of this work, two techniques were tested for this preparation.

When subjecting the potassium trifluoroborate to trimethylsilyl chloride (TMSCl) the desired difluoroborane is formed with trimethylsilyl fluoride (TMSF) and potassium chloride as side products (Scheme 14).[13]

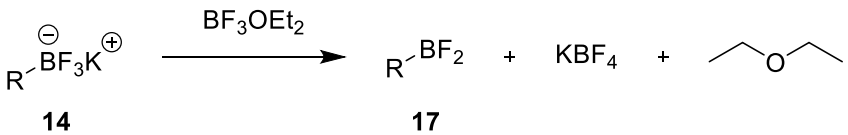



**14** **17**

Scheme 14: Reaction of trifluoroborates with TMSCl

This technique resulted in difficulties analyzing the reaction happening as the stoichiometric/non-stoichiometric role of TMSCl is under question. To avoid that issue another route was chosen to produce the Lewis acid counterparts.

Instead of TMSCl as a fluorine scavenger boron trifluoride diethyl etherate ($BF_3OEt_2$) was used. Here, the imine was subjected to $BF_3OEt_2$ to produce the difluoroborane with potassium tetrafluoroborate and diethyl ether as side products (Scheme 15).[14]

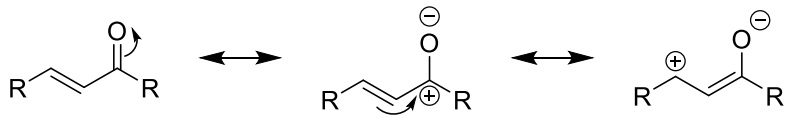



**14** **17**

Scheme 15: Reaction of trifluoroborates with $BF_3OEt_2$

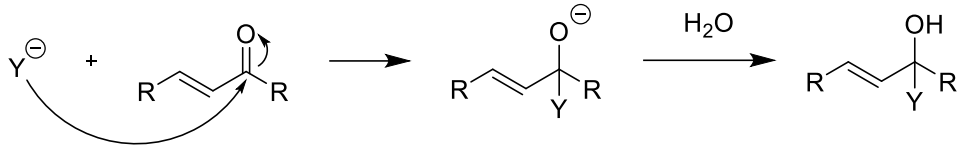
## 1.4 Michael addition (1,4 addition)

When adding a nucleophile to an α,β-unsaturated aldehyde or ketone the nucleophile can attack at two different sites, as the carbonyl compound has two electrophilic sites (Scheme 16).



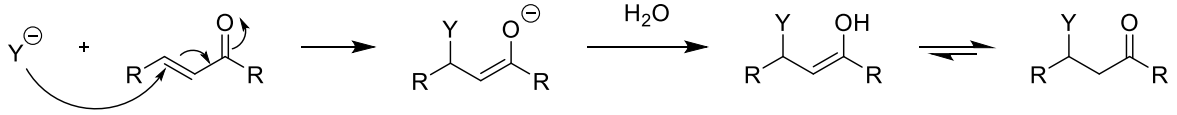
Scheme 16: Electrophilic sites of an α,β-unsaturated carbonyl compound

The nucleophile attacking at the carbonyl carbon results in a 1,2-addition or direct addition (Scheme 17).



Scheme 17: 1,2-addition

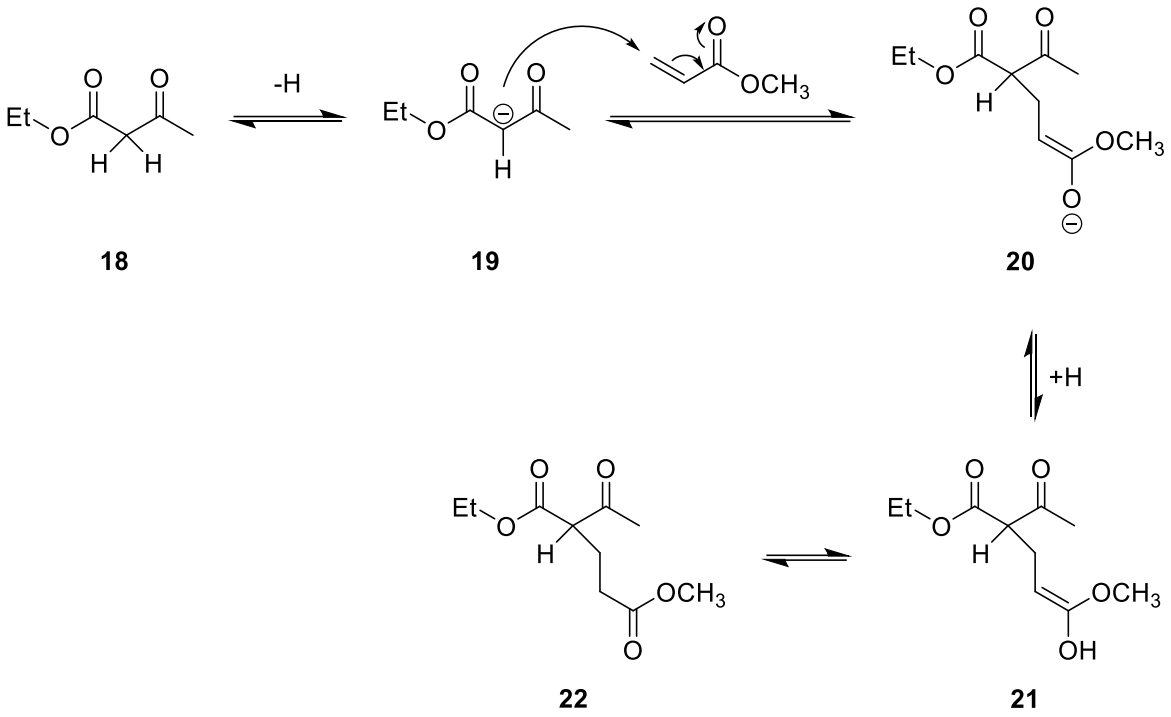
The nucleophilic addition to the β position of the unsaturated compound it is called a 1,4-addtion or also conjugate addition (Scheme 18).[15]



Scheme 18: 1,4-addition

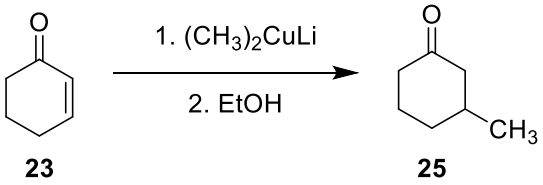
The conjugate addition is also known under Michael reaction, or Michael addition. The nucleophile, termed Michael donor, adds to the carbon atom of a doble bond of the so-called Michael acceptor.

The Michael reaction, which involves the formation of new carbon-carbon bonds, is a widely utilized process in organic chemistry. It is a valuable synthetic method as it allows for the synthesis of various compounds, including drugs, other biologically active substances, and polymers. This reaction has numerous applications in the production of pharmaceuticals and other important materials. In fact, the versatility of the Michael reaction has made it an essential tool in the field of synthetic chemistry. [16]

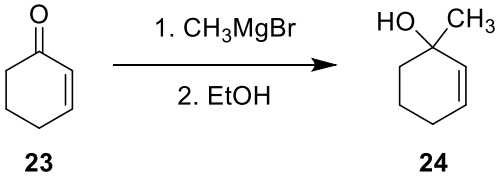



Scheme 19: General mechanism of Michael reaction

Many reactions give both the direct and conjugate addition adducts. The ratio (1,2 vs. 1,4) depends on the participating reagents, temperature, rate of reaction and many more. To ensure only the conjugate addition product a specific organometallic approach is taken. When organocuprates react with α,β-unsaturated carbonyl compounds only the 1,4-addition will take place, as the softer C-Cu bond will attack at the softer carbon-carbon double bond (Scheme 20). In contrast, a Grignard reagent will attack at the harder C=O bond due to the much more polarized C-Mg bond (Scheme 21).[15]

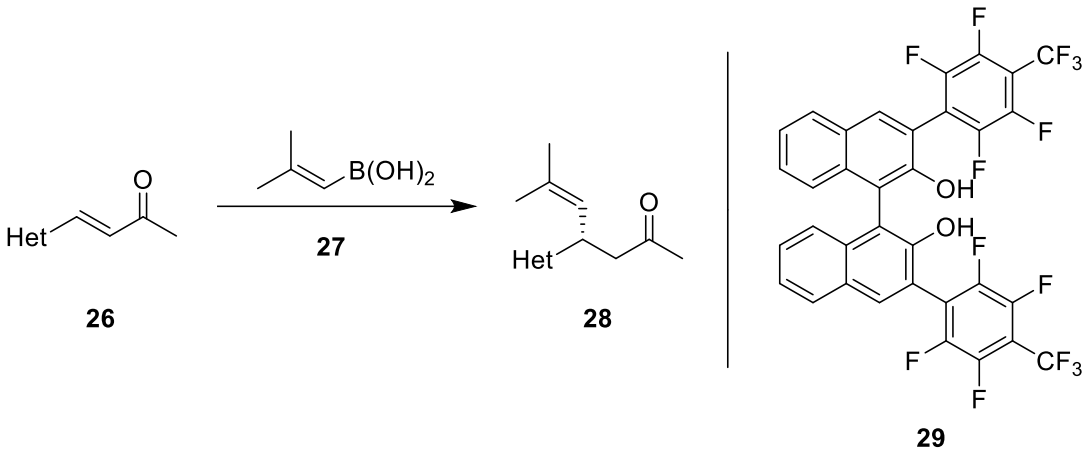



Scheme 20: 1,4-addition with Organocuprates

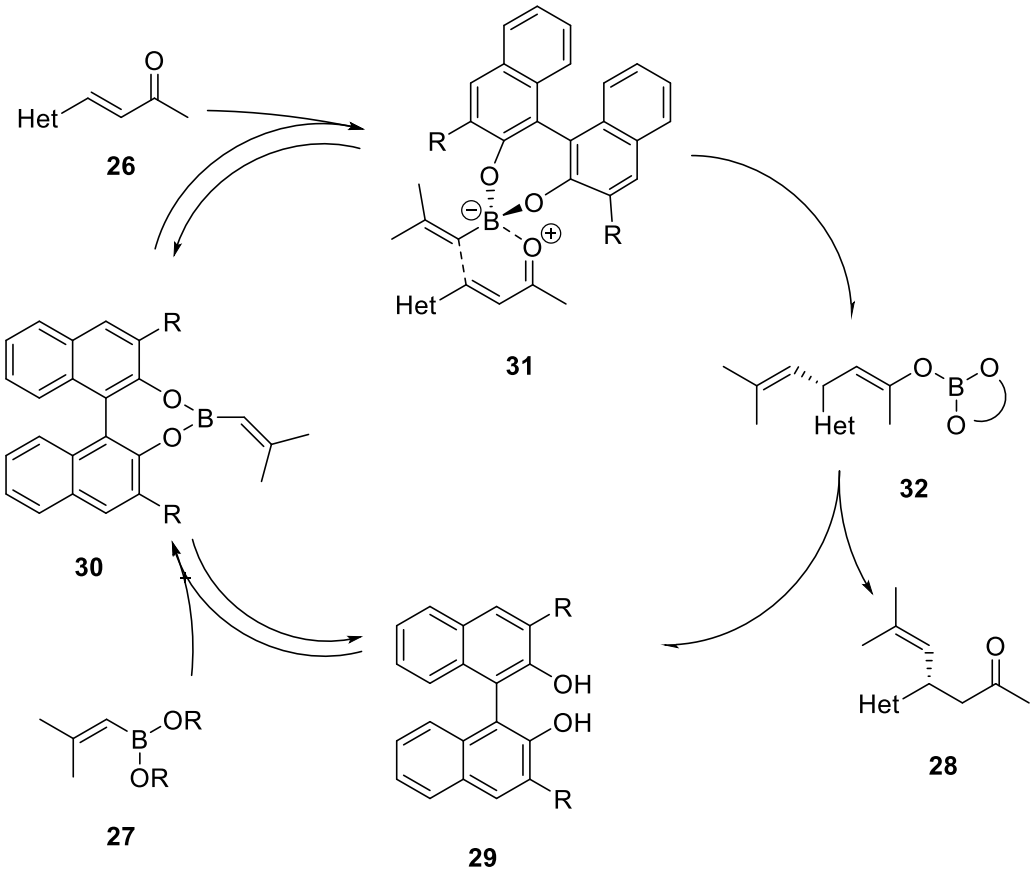



Scheme 21: 1,2-addition with Grignard reagent

May et. al. made use of the 1,4-addition to catalytically add boronic acids to beta-heterocycle-appended enones, as the functionalization of heterocycles is of great importance for the synthesis of natural products and in the pharmaceutical sector. (Scheme 22).



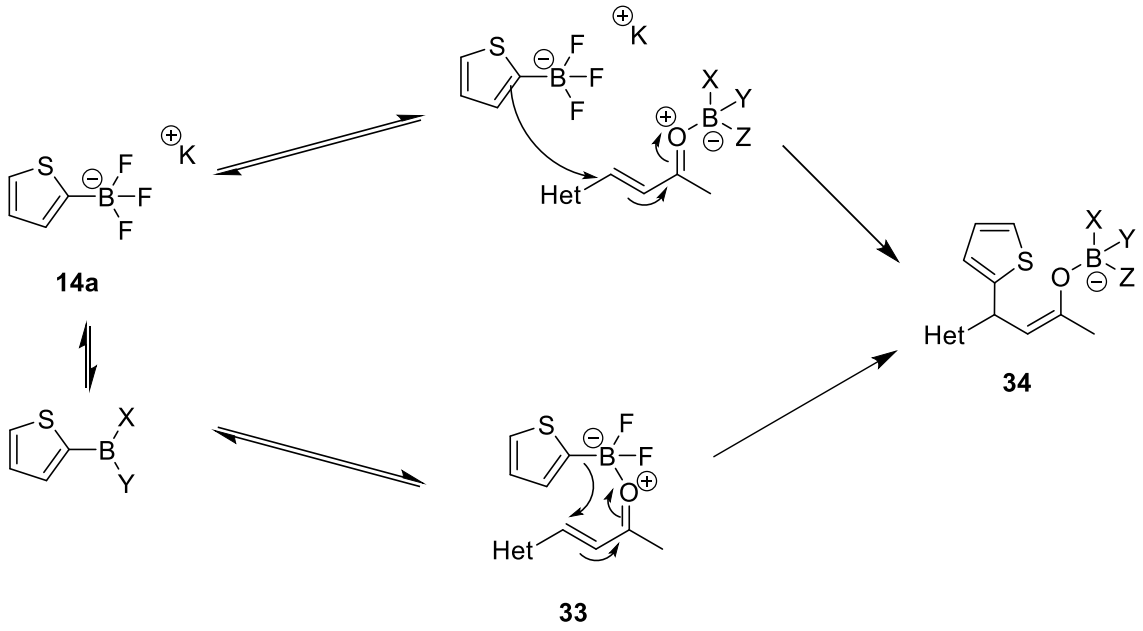

Scheme 22: Goal of May et. al. and catalyst used




Scheme 23: Proposed mechanism for addition (May)

They had to make use of an additive and a fluorinated catalyst due to the rather unreactive carbonyl substrate. The long reaction times it brings with it results in various unwanted side products.[17]

May et al. explored the use of heteroaryl and aryl trifluoroborates as nucleophiles in the 1,4-addition reaction in order to further examine this topic. In their study, they proposed two possible mechanisms for this process (Scheme 24).[4]




Scheme 24: Proposed mechanisms for addition using trifluoroborates (May)

The work of this thesis is strongly inspired by Mays work and the mechanism including complex **33**.

Instead of carbonyl compounds more reactive α,β-unsaturated imines were chosen to be the substrates. This works method is free from a separate preparation of a third-party catalyst. The use of organotrifluoroborates provide an organocatalytic approach to form new carbon-carbon bonds through boron-mediated transfers.

# 2 Objectives

The goal of this research project is to test a new carbon-carbon forming methodology via a boron-mediated transfer. A variety of organotrifluoroborates will be prepared. These will then be subjected to trimethylsilyl chloride (TMSCl) or boron trifluoride diethyl etherate ($BF_3OEt_2$) for in-situ preparation of Lewis acidic organodifluoroboranes. This will form a Lewis acid-base complex with a stock imine that will be synthesized at the beginning.

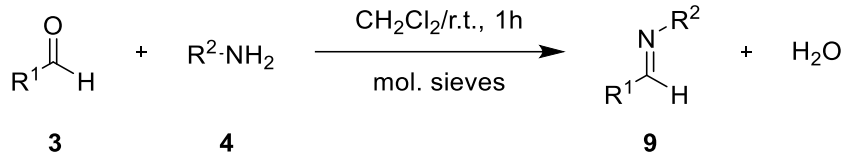
The stock imines will be prepared from their respective aldehydes and amines. The best method for this is to be determined during the course of the research.

After the production of the stock imines the unreactive organoboron compound (Lewis acid) is interacted with an unreactive imine (Lewis base). Those will form a Lewis acid-base complex. This Lewis acid-base interaction and the subsequent nucleophilic boron-mediated transfer of a carbon containing moiety to an electrophilic nitrogen containing counterpart will be evaluated with NMR spectroscopy ($^{11}B$, $^{1}H$).

# 3 Results and Discussion

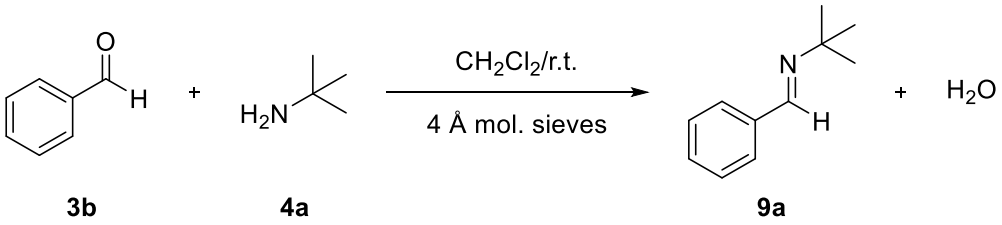
## 3.1 Imine Synthesis

For the synthesis of the starting imines a method already established in this lab was used at first. This method is based on the work of Mangeney et al (Scheme 25).[6] The required imines are prepared from respective aldehydes and primary amines in methylene chloride. Molecular sieves were used to prevent the reaction shifting to the left due to hydrolysis. For additional precaution these reactions were done under nitrogen atmosphere.



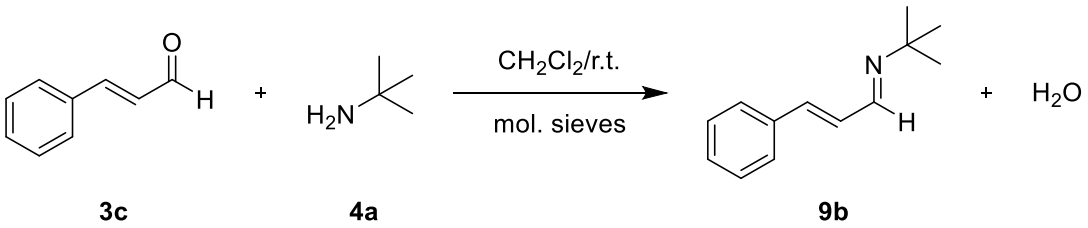

Scheme 25: General synthesis of starting imines (Mangeney)

Applying that method to *trans*-chalcone, a ketone, instead of an aldehyde and *tert*-butylamine (**4a**) did not result in imine formation and only starting material was recovered. Even after heating an aliquot at 50 °C for one hour no change in the NMR spectrum was observed. As a result, the focus was put on aldehyde starting materials. When the same reaction was done with benzaldehyde (**3b**) as a substrate a rather clean spectrum of the product was obtained (Scheme 26).




Scheme 26: Synthesis of benzaldehyde *tert*-butylimine (Mangeney)

To now work with the desired α,β-unsaturated system, *trans*-cinnamaldehyde (**3c**) was used as a starting material for most of the stock imines.

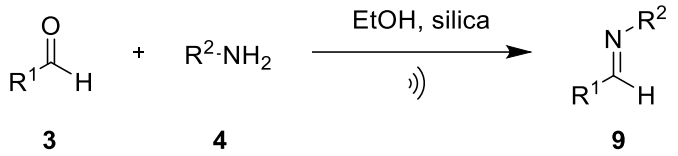



Scheme 27: Synthesis of cinnamaldehyde *tert*-butylimine (Mangeney)

The reaction of *trans*-cinnamaldehyde with *tert*-butyl amine was monitored for completion. After filtering and removing the solvent under reduced pressure the crude product was analyzed by NMR ($^{1}H$, $^{13}C$). Only little starting material and a lot of product was recovered. Because the spectra also contained impurities, especially

around the “*tert*-butyl-region” (1.3 ppm), measures for purifying the compound were taken. Trituration with hexane did not seem to be working, so a column was set up. As the reaction was monitored by TLC and appeared to be susceptible to chromatography, purification by column chromatography was performed to gain experience with that method as well as attempt to purify the compound in that fashion. However, formal column chromatography appeared to hydrolyze the product.

To find a method that does not require purification via column chromatography another approach was taken. The method of Stefani et al. which makes use of ultrasound irradiation and silica as a promoter was applied (Scheme 28).[1]

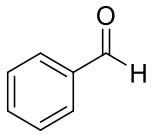
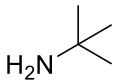
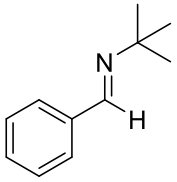
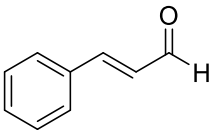
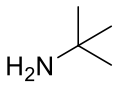
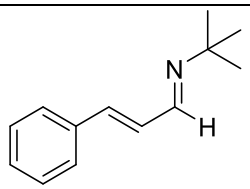
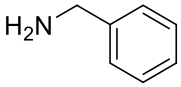
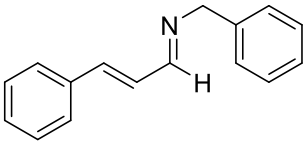
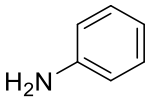
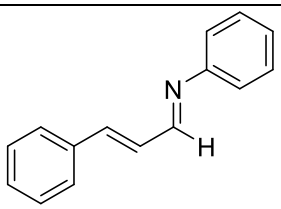



Scheme 28: General synthesis of starting imines (Stefani)

After solvent removal under reduced pressure ethanol was still prominent in the NMR spectra using this method. To get rid of any residual solvent acetonitrile was added for azeotropic removal of ethanol.

Different starting materials were used to generate the respective imines (**9a-9d**) in the same manner (Table 1).

Table 1: Different imine products

| Entry | Aldehyde (**3**) | Amine (**4**) | Imine (**9**) |
|---|---|---|---|
| 1 |  **3b** |  **4a** |  **9a** |
| 2 |  **3c** |  **4a** |  **9b** |
| 3 | **3c** |  **4b** |  **9c** |
| 4 | **3c** |  **4c** |  **9d** |

For comparison of following experiments, the reaction was done with benzaldehyde (**3b**) and *tert*-butylamine (**4a**) first. As expected, this reaction delivered very clean spectra of the product with very precise integration ratios.

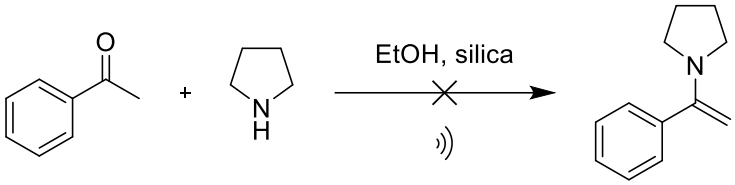
For the cinnamaldehyde *tert*-butylimine (**9b**) using a 1:1 ratio of the starting materials delivered a very clean $^{1}$HNMR spectrum, which still shows about 10 % of starting aldehyde. As a result, two equivalents of the amine **4a** were used to avoid the presence of unreacted staring aldehyde. As *tert*-butylamine has a boiling point of 46 °C it vanishes on the pump when removing the solvent under reduced pressure. With that reaction even on bigger scales, up to 20 mmol, no further purification was necessary as it delivers very clean spectra.

After trying different rations for the production of cinnamaldehyde benzylimine (**9c**), using 1.2 equivalents of the amine **4b** appeared to be the best ratio to avoid starting aldehyde in the product. The method delivered relatively clean spectra at first with only very little of the starting amine and ethanol. After trying to remove the residual solvent with acetonitrile the spectrum shows a lot of impurities. A method to remove

the ethanol differently or to purify the product after azeotropic removal is yet to be determined.

Doing the same rection with phenyl amine (**4c**), aniline, for the production of cinnamaldehyde phenylimine (**9d**) resulted in a yellowish reaction mixture sludge. For still being able to filtrate the silica off, the reaction mixture was dissolved in methylene chloride. The reaction delivered a good spectrum with only minor impurities.

Two entirely different starting materials were chosen to test the limitations of this method, namely acetophenone and pyrrolidine. This reaction should result in the production of the respective enamine. Unfortunately, after performing the reaction in the same manner as the production of the imines, only starting materials were recovered. Even after adding a catalytic amount of acid to push the reaction forward, no reaction was observed. Due to time constraints no more investigations were done in that direction. Even though the two conducted attempts were not successful, this topic is worth looking into in the future (Scheme 29).




Scheme 29: Enamine formation

## 3.2 Boron-Mediated Transfers

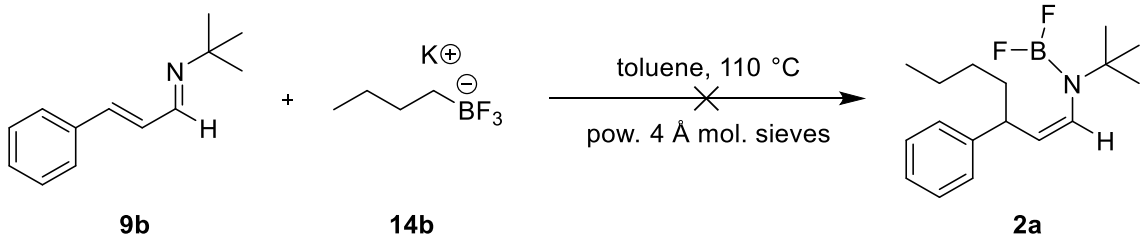
Initially, experiments with a variety of different reactants were examined, including benzylimine, phenylimine and phenyl trifluoroborate. Due to several reasons, like purity and availability, the focus was put on using cinnamaldehyde *tert*-butylimine, butyl trifluoroborate and allyl trifluoroborate as starting materials.

### 3.2.1 Transfer of butyl group

The decision on aiming for a butyl transfer was influenced by the readily availability of butyl trifluoroborate and the respective boronic acid. Moreover, the objective was not limited to transferring an allyl group, since transferring a butyl group presents more of a challenge. Gathering information on a butyl transfer would be of great importance, because a successful transfer of a butyl group could indicate the transferability of several other groups as well.

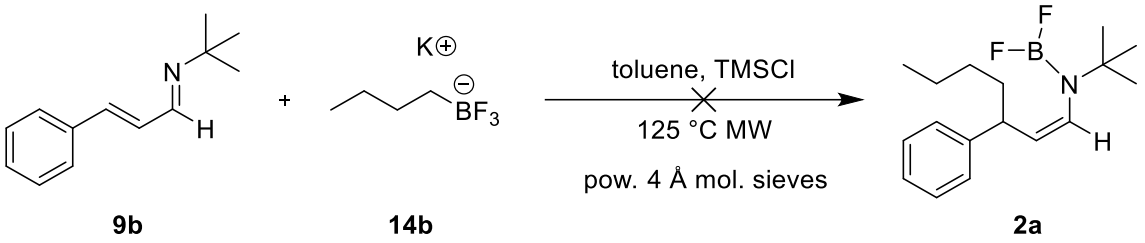
For the first try of a boron-mediated transfer of a butyl group all the reagents were simply put into an NMR reaction tube with deuterated chloroform as a solvent. The potassium butyl trifluoroborate is not soluble in this solvent, but the respective difluoro compound is. After the addition of TMSCl first shifts in the imine region of the proton NMR could already be observed. Additionally, now that the butyl containing compound is soluble, also peaks in the lower area of the spectrum were observed. Also in that area, TMS peaks were showing up. The boron and fluorine spectra are indicators that some reaction was happening. A shift to the difluoro compound (28.61 ppm) could be observed. On the other hand, that peak could also indicate a boron with two different heteroatoms, like butyl boronic acid. In addition, also a sharp peak at -1.7 ppm indicates the formation of an ate-complex. The fluorine spectrum shows the distinct TMSF peak (-157.59 ppm) and two other new peaks. Already from that simple experiment, we can conduct, that something is happening in the NMR tube but for better understanding what reactions are occurring further experiments have to be done.

May et. al. conducted similar research which includes the addition of different boronic acids to enones.[17,18] Mimicking his work as best as possible a new set up for this reaction was chosen (Scheme 30).




Scheme 30: Butyl transfer: Mimicking the work of May et.al.

After running this reaction for 9.5 h in the monowave only the starting imine was recovered after filtering the liquid from the molecular sieves. Even after using 4 equivalents of butyl trifluoroborate to ensure enough reagent, no reaction was observed. For that reason, TMSCl was used again to help driving the reaction forward (Scheme 31).

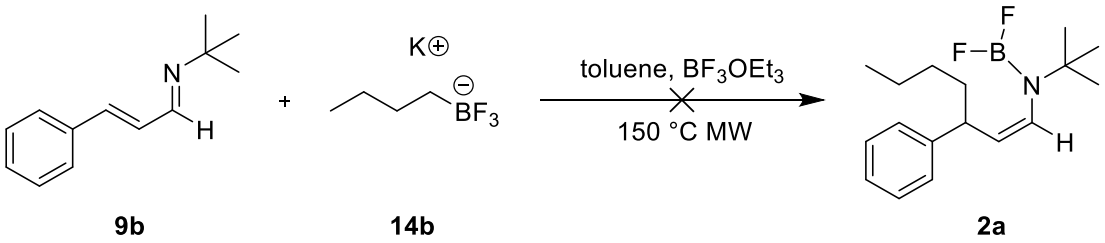



Scheme 31: Butyl transfer: Adding TMSCl as a reaction partner

Having the reaction now in the microwave for 6 h at 125 °C seems to not affect the imine part of the spectrum, but only new butyl peaks are visible. The boron spectrum shows again a peak at 31.71 ppm indicating the presence of a boron with two hetero atoms. As there is no peak in the fluorine spectrum it is most likely a boronic acid. To test this $KHF_2$ was added to the reaction mixture and a shift back to the expected trifluoro compound was observed in the boron as well as in the fluorine spectrum.

As May uses boronic acids in his experiments, butyl boronic acid was chosen for a comparison experiment. As this delivered very similar results as with the respective trifluoro borate, $KHF_2$ was added here as well. However, here only a partly shift to the trifluoro compound was observed.

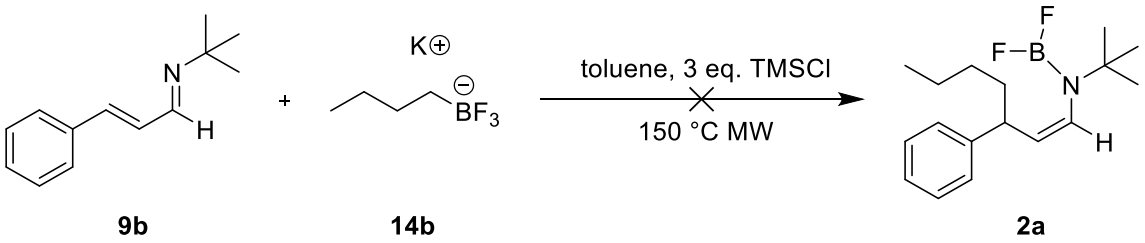
Doubting that TMSCl only acts as a fluorine scavenger in that reaction, $BF_3OEt_2$ was chosen to act as a scavenger instead (Scheme 32). Immediate change in colour and flocculation was observed when adding the etherate to the reaction mixture.




Scheme 32: Butyl transfer: Boron trifluoride diethyl etherate as fluorine scavenger

After heating it for 90 min in the microwave, still a broad peak around 0 ppm was observed in the proton spectrum, which is a typical sign for the two hydrogen atoms right next to the boron on the trifluoroborate. Even after adding MeOH to rule out solubility issues the peak remains. Only after adding one equivalent of TMSCl to the reaction mixture this changed.

Knowing this, excess TMSCl (3 eq.) was used for the next experiment (Scheme 33).




Scheme 33: Butyl transfer: 3 equivalences of TMSCl

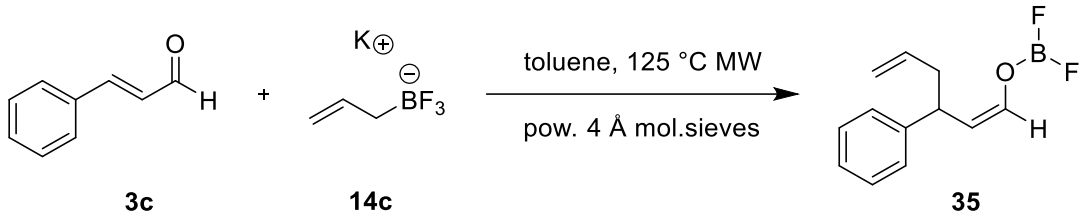
After 4.5 h in the microwave both the imine and butyl peaks were visible in the proton spectrum. The boron spectrum showed similar peaks as with previous experiments – the respective difluoro compound or a boron with two other hetero atoms, the starting trifluoroborate and an ate-complex at -1.88 ppm. Also the fluorine spectrum shows two prominent peaks at -148.78 and -148.83 ppm. As of now it is believed that this is due to an ate-complex formation with a TMS counterpart. To the reaction mixture water was added to get more understanding of the reaction happening. Now the imine was completely hydrolysed and only the starting cinnamaldehyde and butyl peaks were observed. Further, no *tert*-butyl group was detected as the respective amine has a relative low boiling point and is removed on the rotary evaporator. The boron spectrum only shows a peak at 32.02 ppm and no fluorine peak was detected as it came off as TMSF on the pump. After a column rather pure cinnamaldehyde was separated from the butyl compound, which was not the starting trifluoroborate but presumably butyl boronic acid, as we see the respective peak in the boron spectrum and no fluorine.

To take a step back the butyl transfer was attempted by using benzaldehyde *tert*-butylimine instead of the unsaturated system. The same procedure was applied here and removing an aliquot showed similar results as before. Interestingly, during the reaction perfectly round solid pellets have formed and overnight flakes appeared also. After investigating all three components it became clear that the solid is most probably something inorganic as it only dissolves in $D_2O$ and does not show up in NMR spectra, presumably during the reaction formed KCl. The flakes turned out to have a clean, starting imine similar, proton NMR spectrum. Small shifts were observed but the integration fits the imine protons. However, in the boron spectrum we see the ate-complex at -1.80 ppm and in the fluorine spectrum at -148.94 and -149.00 ppm. The liquid itself does not show any imine peaks, only butyl. No fluorine was detected but next to the peak for the boronic acid, an interesting new peak at 17.56 ppm appeared in the boron spectrum.

Even though a successful transfer was not recorded, these experiments yielded valuable data. As the role of TMSCl in these experiments is not fully understood this can act as a good basis for further research on this topic, as this is worth to be further investigated.

### 3.2.2 Transfer of allyl group

To begin with, we replicated the method of May et al. as best as possible and used cinnamaldehyde as the substrate for our first attempt at transferring an allyl group (Scheme 34).

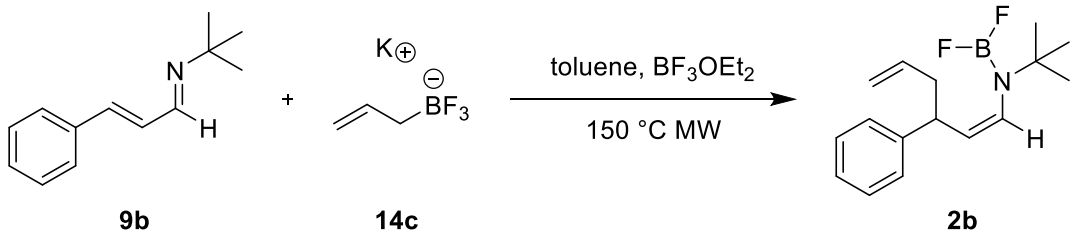



Scheme 34: Allyl transfer: Mimicking the work of May et.al.

After having the reaction for 6 h on the microwave, no starting material was detected in the aliquot that was removed, indicating that a reaction is happening. Additionally, neither a boron nor a fluorine was detected by NMR analysis. After filtering the reaction mixture and rinsing it with ethyl acetate the liquid was treated with dichloromethane to get a cleaner spectrum. Afterwards small possible allyl peak could be observed. After a column was done there were still some promising allyl peaks present, but the spectrum itself got very messy. The filtration solid got again washed with methanol. Careful NMR analysis of that sample showed the presence of only starting allyl trifluoroborate. Although the transfer could not be fully proven, this experiment provided promising evidence of the transfer.

Repeating the same experiment using *tert*-butylimine as the reactant resulted in the reaction being burned. A new, research-grade microwave was used, and a temperature of 250 °C was maintained for 1.5 hours. Interestingly, when analyzing the now black liquid it seems that it contains the pure starting imine, which indicates a great stability of the imine but nothing else happening.

Given that promising data had already been established but the conditions were not optimal, it was decided to modify the conditions. The role of the molecular sieves was still unclear at that moment. Therefore, $BF_3OEt_2$ was used as a fluorine scavenger to drive the reaction forward (Scheme 35).

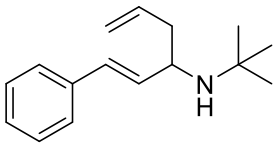



Scheme 35: Allyl transfer: $BF_3OEt_2$ as fluorine scavenger

During reaction monitoring after only 1 h 45 min in the microwave the NMR analysis of an aliquot showed signs of the product. After the solvent removal under reduced pressure the sample was being dissolved in toluene again for column chromatography. Not everything went into solution and a residue was left on the bottom. The column was still done, but it delivered very messy spectra. Although,

the allyl peaks could still be observed. Upon analysis of the residual, a clear spectrum of all expected components was obtained. This sample was put through an NMR exercise in order to gather additional data on the suspected product. After adding MeOH and $D_2O$ to the sample, each time the splitting of the peaks increased. When adding HCl to it, the splitting went back to how it was in the beginning. Separating the organic from the aqueous phase, the product in the organic phase showed a minor hydrolysis. The spectrum also showed the presence of two different *tert*-butyl peaks. This assumption was strengthened by a carbon NMR analysis. Also worth mentioning is the boron spectrum, as it shows a sharp peak at -1.85 ppm, indicating an ate-complex. In connection with that, two peaks at -146.96 ppm and -147.02 ppm were observed in the fluorine spectrum.

Running the same reaction again attempting to obtain more product led to very similar results in the beginning. After the short reaction time, all the allyl peaks could be observed in the NMR spectrum. Although, at that point in the reaction mixture contained three different types of *tert*-butyl peaks in the proton as well as in the respective carbon NMR spectrum. When trying to dissolve the reaction mixture again in toluene, an insoluble residue remained at the bottom of the vial. Analyzing the residue first, a very promising spectrum was acquired but still, three different kinds of *tert*-butyl peaks were present. For purifying the compound, a column was set up. On the column it got separated from something that appeared to be hydrolyzed and got cleaner in general. Only one peak did not integrate in the right way, but after adding $D_2O$, it got clear that this was only because of interchangeable protons. At this stage, only two different *tert*-butyl peaks were observed in the reaction mixture. To get an even cleaner product a second column was done. In doing so, a very clean product could be obtained. No boron or fluorine was observed. Further careful NMR analysis confirmed the successful transfer of an allyl group to an imine. But it was not the expected product drawn in Scheme 35Figure 1, but rather the allyl group attached to the imino-carbon (Figure 1).



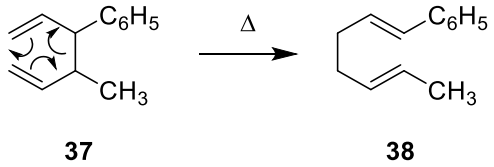

**36**

Figure 1: Product of allyl transfer

As the liquid seemed to have the same contents as the residue, also two columns were performed to get a clean product. In the end, there was still a boron and fluorine peak in their respective spectra, but by adding extra $BF_3OEt_2$ it was confirmed that the peaks were due to excess $BF_3OEt_2$.

Two different reaction mechanisms leading to the same product are possible. The first mechanism proposes a boron-mediated 1,5 transfer to the beta-position of the imine first with a subsequent Cope rearrangement forming the product. A Cope rearrangement is a type of chemical reaction that involves the [3,3] sigmatropic rearrangement of a 1,5-diene. It involves the breaking of a sigma bond in the reactant, the formation of a new sigma bond, and the rearrangement of the pi

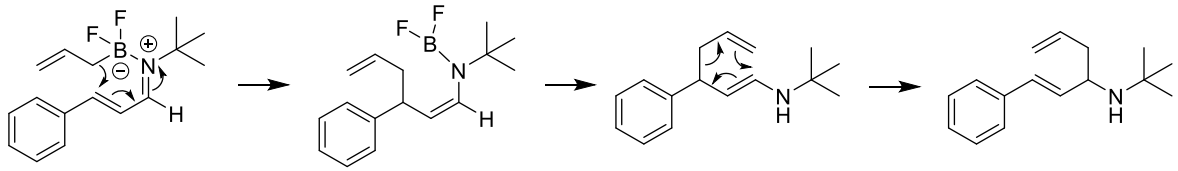
electrons. This reaction typically takes place under thermal conditions and forms a six-membered transition state (Scheme 36Scheme 36: Cope rearrangement).[15]



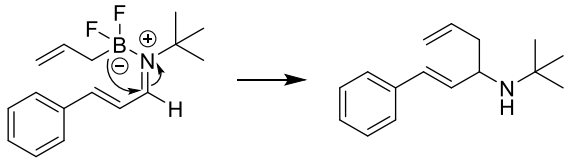

**37** **38**

Scheme 36: Cope rearrangement

The second mechanism shows a boron-mediated 1,3 transfer.




**1a** **2a** **39** **36**




**1a** **36**

Scheme 37: Two possible reaction mechanisms for allyl transfer

This successful transfer is a great addition to organic reaction methodology and can serve as the foundation for further research in this area.

# 4 Conclusions

The initial aimed for functionalization of the β-position of an α,β-unsaturated imine was not confirmed, as we see other or further reactions happening when transferring an allyl group. Nevertheless, this provides important data and adds greatly to reaction methodology. The evidence of the successful allyl transfer will serve as the jumping off point for further research in this area.

Even though a successful butyl transfer was not recorded, these experiments also yielded valuable data and can act as a good basis for further research on this topic, as this is worth to be further investigated.

In conclusion, this work brings new methodology to the field that is free from metallic catalysis. It opens up the possibility for more environmentally friendly approaches to carbon-carbon bond formation and sets the stage for future research in the field.

# 5 Experimental

## 5.1 General and instrument details

The chemicals were purchased from Sigma Aldrich and used without further purification.

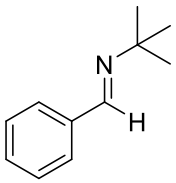
A JEOL JNM-ECP 400 FT-NMR spectrometer was used, which provided H-NMR (400 MHz), C-NMR (101 MHz), B-NMR (128 MHz) and F-NMR (376 MHz)

Monowave: Anton Paar, Monowave 50+P, P/N: 168600, S/N: 81991198

Microwave: Anton Paar, Microwave Synthesis Reactor, Monowave 400, P/N: 163523, S/N: 83937941

Ultrasonic Cleaner: PNKKODW Digital Ultrasonic Cleaner, Model: TH-20A

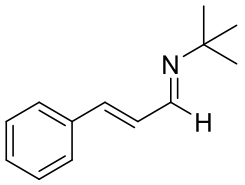
## 5.2 Benzaldehyde *tert*-butylimine (Mangeney)




**9a**

A clean and dry 50 mL round bottom flask was charged with benzaldehyde (3 mmol, 0.3 mL) and $CH_2Cl_2$ (15 mL). To that molecular sieves were added. This stirred mixture was put under nitrogen atmosphere before *tert*-butylamine (1 eq., 0.3 mL) was added dropwise through a septum. The reaction was monitored by TLC and NMR on completion. The resulting solution was filtered through a fritted funnel and concentrated to give crude product which was characterized by NMR. **Yield**: 76.6 %; **$^1$H NMR** (400 MHz, CHLOROFORM-D) δ 8.26 (s, 1H), 7.76 (s, 2H), 7.39 (p, *J* = 3.3 Hz, 3H), 1.30 (s, 9H); **$^{13}$C NMR** (101 MHz, CHLOROFORM-D) δ 128.66, 128.12, 29.76.

## 5.3 Cinnamaldehyde tert-butylimine (Mangeney)

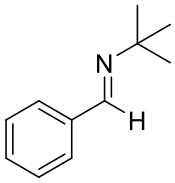


**9b**

A clean and dry 50 mL round bottom flask was charged with *trans*-cinnnamaldehyde (3 mmol, 0.38 mL) and $CH_2Cl_2$ (15 mL). To that molecular sieves were added. This stirred mixture was put under nitrogen atmosphere before *tert*-butylamine (1 eq., 0.3 mL) was added dropwise through a septum. The reaction was monitored by TLC and NMR on completion. The resulting solution was filtered through a fritted funnel and concentrated to give crude product which was characterized by NMR. **Yield**: 82.95 %; **$^1$H NMR** (400 MHz, CHLOROFORM-D) δ 8.06 – 8.00 (m, 1H), 7.54 – 7.26 (m, 7H), 6.98 (s, 2H), 5.28 (s, 1H), 1.27 (d, *J* = 2.1 Hz, 10H).

For further purification a column was done (3:1, hexane:ethylacetate). The product was not susceptible to formal column chromatography, as it appeared to hydrolyze the product. **$^1$H NMR** (400 MHz, CHLOROFORM-D) δ 9.70 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.47 (m, 3H), 7.50 – 7.38 (m, 4H), 7.38 – 7.29 (m, 0H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H), 1.42 (s, 1H), 1.48 – 1.16 (m, 2H), 1.23 (s, 7H), 0.88 (s, 4H), 0.97 – 0.76 (m, 3H).

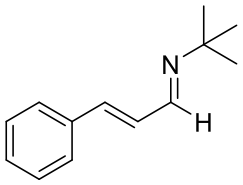
## 5.4 Benzaldehyde *tert*-butylimine (Stefani)



**9a**

A clean and dry 25 mL round bottom flask was charged with silica (5 eq., 1.5 g), benzaldehyde (5 mmol, 0.5 mL), ethanol (8.5 mL) and *tert*-butylamine (2 eq., 1 mL). This was irradiated in the water bath of the ultrasonic cleaner at 21 °C for 30 min. The resulting solution was filtered through a fritted funnel containing celite and the solvent was removed under reduced pressure. Residual ethanol was azeotropically removed with acetonitrile. The product was analyzed and characterized by NMR. **Yield**: 99.55 %; **$^1$H NMR** (400 MHz, CHLOROFORM-D) δ 8.26 (s, 1H), 7.74 (dd, *J* = 6.8, 3.1 Hz, 2H), 7.38 (dd, *J* = 5.0, 2.0 Hz, 3H), 1.29 (s, 9H).

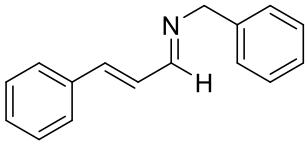
## 5.5 Cinnamaldehyde *tert*-butylimine (Stefani)



**9b**

A clean monowave tube was charged with silica (5 eq., 900 mg), cinnamaldehyde (3 mmol, 0.38 mL), *tert*-butylamine (2 eq., 0.63 mL) and ethanol (5 mL). This was then irradiated in the water bath of the ultrasonic cleaner at room temperature (21 °C) for 10 minutes. The resulting solution was filtered through a fritted funnel containing celite and the solvent was removed under reduced pressure. Residual ethanol was azeotropically removed with acetonitrile. The product was analyzed and characterized by NMR. **Yield**: 86.85 %; **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.03 (dd, *J* = 4.7, 3.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.25 (m, 3H), 6.95 (d, *J* = 3.8 Hz, 2H), 1.25 (s, 9H); **$^{13}$C NMR** (101 MHz, CHLOROFORM-D) δ 157.64, 135.97, 129.16, 128.92, 127.33, 57.38, 29.74.

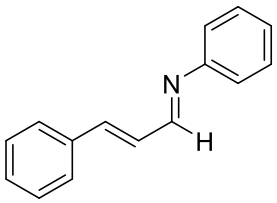
## 5.6 Cinnamaldehyde benzylimine (Stefani)



**9c**

A clean monowave reaction tube was charged with silica (5 eq., 3 g), cinnamaldehyde (10 mmol, 1.26 mL), benzylamine (1.2 eq., 1.3 mL) and ethanol (17 mL). This was then irradiated in the water bath of the ultrasonic cleaner at 21 °C for 60 minutes. The resulting solution was filtered through a fritted funnel containing celite and the solvent was removed under reduced pressure. Residual ethanol was azeotropically removed with acetonitrile. The product was analyzed and characterized by NMR. **Yield**: 96.20 %; **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.15 (ddt, *J* = 4.7, 3.0, 1.4 Hz, 1H), 7.73 – 7.57 (m, 1H), 7.57 – 7.34 (m, 5H), 7.38 – 7.29 (m, 5H), 7.33 – 7.24 (m, 1H), 7.28 – 7.21 (m, 1H), 7.24 – 7.15 (m, 1H), 7.19 – 7.09 (m, 1H), 7.09 – 6.92 (m, 2H), 4.73 (d, *J* = 1.4 Hz, 2H), 4.27 – 4.11 (m, 0H), 4.05 (s, 0H), 3.93 – 3.72 (m, 0H), 3.63 – 3.52 (m, 0H), 1.97 (s, 0H), 2.01 – 1.85 (m, 0H); **$^{13}$C NMR** (101 MHz, CHLOROFORM-D) δ 163.61, 142.18, 139.58, 139.30, 138.99, 135.81, 129.39, 129.35, 128.98, 128.80, 128.71, 128.48, 128.40, 128.38, 128.31, 128.22, 127.99, 127.73, 127.39, 127.30, 127.19, 126.95, 126.81, 126.74, 126.58, 70.09, 66.24, 65.88, 65.41, 64.11, 59.87, 59.41, 57.97, 54.76, 53.93, 52.46, 37.46, 32.37, 31.55.

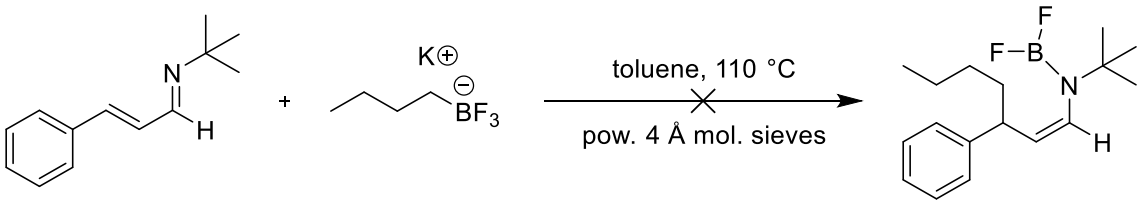
## 5.7 Cinnamaldehyde phenylimine (Stefani)



**9d**

A clean monowave reaction tube was charged with silica (5 eq., 3 g), cinnamaldehyde (3 mmol, 0.38 mL), phenylamine (1.2 eq., 0.33 mL) and ethanol (5 mL). This was then irradiated in the water bath of the ultrasonic cleaner at 21 °C for 10 minutes. Methylene chloride was added to the solution as a precipitate was formed. The resulting solution was filtered through a fritted funnel containing celite and the solvent was removed under reduced pressure. Residual ethanol was azeotropically removed with acetonitrile. The product was analyzed and characterized by NMR. **Yield**: 97.73 %; **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.33 – 8.20 (m, 1H), 7.58 – 7.49 (m, 2H), 7.52 – 7.27 (m, 6H), 7.31 – 7.10 (m, 6H), 6.79 – 6.62 (m, 1H); **$^{13}$C NMR** (101 MHz, CHLOROFORM-D) δ 161.77, 129.38, 129.09, 127.82, 121.01.

## 5.8 Butyl transfer mimicking May et.al. (w/o TMSCl)

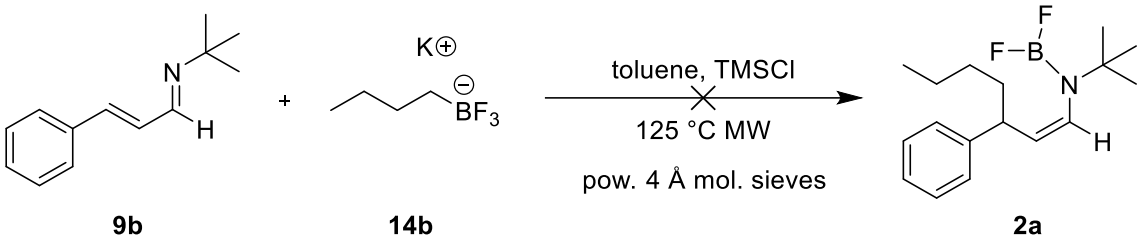



**9b** **14b** **2a**

A monowave reaction tube was charged with 4 Å powdered molecular sieves (0.5 g), potassium butyltrifluoroborate (4 eq., 0.656 g), cinnamaldehyde *tert*-butyl imine (1 mmol, 0.187 g) and toluene (4 mL). This was heated for 9.5 h at 110 °C in the monowave. The reaction was filtered through a fritted funnel and the solvent was removed under reduced pressure. The product was analyzed and characterized by NMR. Only starting imine was recovered. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.03 (dd, *J* = 4.7, 3.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.25 (m, 3H), 6.95 (d, *J* = 3.8 Hz, 2H), 1.25 (s, 9H).

Failed synthesis

## 5.9 Butyl transfer with TMSCl



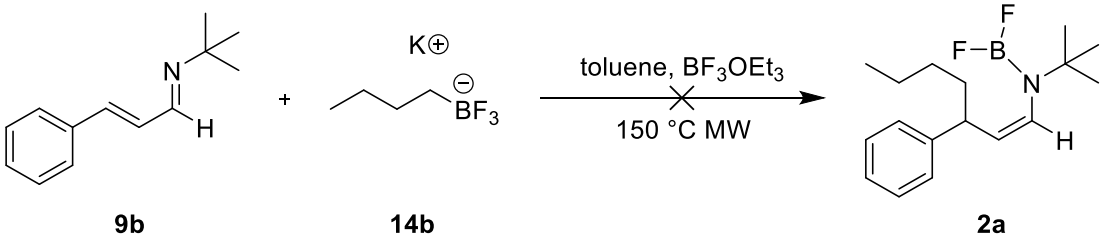

**9b** **14b** **2a**

A microwave reaction tube was charged with 4 Å powdered molecular sieves (0.5 g), potassium butyltrifluoroborate (1.2 eq., 0.197 g), cinnamaldehyde *tert*-butylimine (1 mmol, 0.187 g) and toluene (3 mL). This was heated for 6 h at 125 °C in the microwave. NMR analysis of a reaction aliquot was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.03 (t, *J* = 4.1 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.38 – 7.19 (m, 4H), 6.95 (d, *J* = 4.0 Hz, 2H), 1.44 – 1.16 (m, 13H), 1.25 (s, 10H), 0.88 (h, *J* = 7.7 Hz, 2H), 0.17 – 0.03 (m, 1H); **$^{11}$B NMR** (128 MHz, CHLOROFORM-D) δ 31.71.

After adding KHF2 another NMR analysis was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.07 – 8.00 (m, 1H), 7.59 – 7.39 (m, 3H), 7.42 – 7.27 (m, 3H), 7.04 (p, *J* = 4.2 Hz, 2H), 4.92 – 4.79 (m, 14H), 3.00 (s, 3H), 1.28 (d, *J* = 2.6 Hz, 11H), 0.88 (dt, *J* = 20.3, 7.1 Hz, 1H); **$^{11}$B NMR** (128 MHz, CHLOROFORM-D) δ 2.58 (d, *J* = 792.2 Hz); **$^{19}$F NMR** (376 MHz, CHLOROFORM-D) δ -115.97 – -122.62 (m), -133.30, -143.43, -157.60 (dd, *J* = 14.7, 5.7 Hz).

Failed synthesis

## 5.10 Butyl transfer with BF3OEt2




**9b** **14b** **2a**

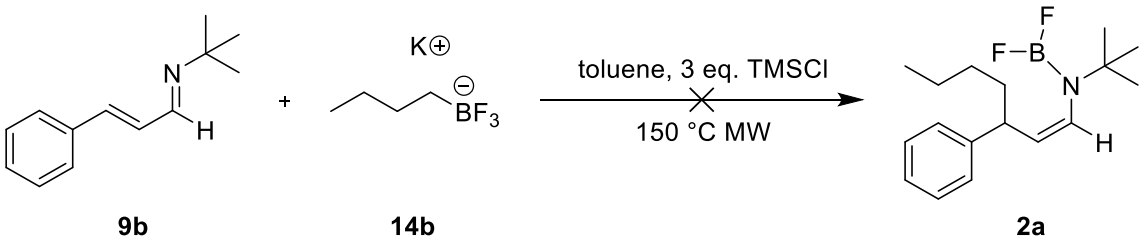
A microwave reaction tube was charged with potassium butyltrifluoroborate (1 eq., 0.328 g), cinnamaldehyde *tert*-butylimine (2 mmol, 0.374 g), toluene (4 mL) and $BF_3OEt_2$ (1 eq., 0.25 mL). This was heated for 1 h 30 min at 150 °C in the microwave. NMR analysis of a reaction aliquot was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.53 – 8.47 (m, 1H), 8.27 (s, 0H), 7.78 – 7.70 (m, 1H), 7.59 – 7.44 (m, 1H), 7.47 – 7.29 (m, 3H), 7.33 – 7.24 (m, 1H), 7.28 – 7.13 (m, 5H), 7.14 (dd, *J* = 6.3, 3.5 Hz, 1H), 7.03 – 6.96 (m, 0H), 6.96 – 6.87 (m, 1H), 4.21 (s, 0H), 3.98 (s, 1H), 2.35 (s, 2H), 1.37 (s, 1H), 1.37 (s, 7H), 1.29 (s, 4H), 1.35 – 1.15 (m, 5H), 0.97 – 0.82 (m, 2H), 0.86 – 0.77 (m, 1H), 0.28 (h, *J* = 7.5 Hz, 2H); **$^{11}$B NMR** (128 MHz, CHLOROFORM-D) δ 5.63, -2.03; **$^{19}$F NMR** (376 MHz, CHLOROFORM-D) δ -131.81, -150.03 (d, *J* = 20.1 Hz), -154.12.

After adding 0.5 mL of MeOH another NMR analysis was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 9.04 (ddd, *J* = 21.1, 5.9, 1.9 Hz, 1H), 8.52 – 8.43 (m, 1H), 7.90 (d, *J* = 6.6 Hz, 1H), 7.83 – 7.70 (m, 1H), 7.59 – 7.31 (m, 6H), 7.31 – 7.10 (m, 9H), 7.02 – 6.95 (m, 1H), 6.95 – 6.89 (m, 1H), 4.21 (s, 1H), 3.97 (s, 1H), 2.34 (s, 3H), 1.71 (s, 4H), 1.44 – 1.18 (m, 17H), 0.85 (t, *J* = 6.9 Hz, 3H), 0.27 (h, *J* = 7.6 Hz, 2H); **$^{11}$B NMR** (128 MHz, CHLOROFORM-D) δ 2.54 (d, *J* = 782.8 Hz), -2.00; **$^{19}$F NMR** (376 MHz, CHLOROFORM-D) δ -131.65, -140.98 (d, *J* = 29.4 Hz), -149.91 (d, *J* = 19.7 Hz), -154.07.

After adding 1 eq. of TMSCl another NMR analysis was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.68 – 8.51 (m, 1H), 8.36 (s, 1H), 7.90 – 7.80 (m, 1H), 7.80 – 7.64 (m, 1H), 7.59 – 7.49 (m, 1H), 7.45 (dddd, *J* = 16.1, 9.3, 4.5, 1.4 Hz, 4H), 7.35 (dddd, *J* = 17.0, 8.8, 4.6, 1.6 Hz, 1H), 7.31 – 7.08 (m, 10H), 7.03 – 6.91 (m, 1H), 6.95 – 6.88 (m, 1H), 4.49 (s, 1H), 4.03 (s, 1H), 3.53 (d, *J* = 8.3 Hz, 1H), 3.44 (s, 1H), 3.31 (s, 1H), 2.33 (s, 3H), 1.78 (s, 2H), 1.49 (s, 1H), 1.44 (s, 4H), 1.39 – 1.27 (m, 1H), 1.29 (s, 3H), 0.95 – 0.77 (m, 2H), 0.74 (d, *J* = 7.7 Hz, 1H), 0.20 – 0.08 (m, 1H), 0.12 – 0.04 (m, 2H), 0.06 (s, 17H); **$^{11}$B NMR** (128 MHz, CHLOROFORM-D) δ 31.29, -2.01; **$^{19}$F NMR** (376 MHz, CHLOROFORM-D) δ -130.60 (h, *J* = 6.5 Hz), -151.30, -151.35, -154.10.

Failed synthesis

## 5.11 Butyl transfer with 3eq. TMSCl




**9b** **14b** **2a**

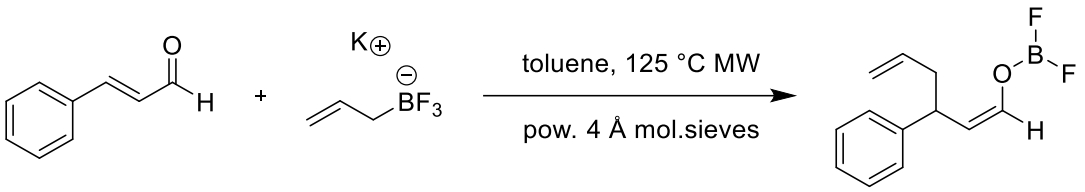
A microwave reaction tube was charged with potassium butyltrifluoroborate (1.2 eq., 0.5904 g), cinnamaldehyde *tert*-butylimine (3 mmol, 0.0.561 g), toluene (4 mL) and TMSCl (3 eq., 1.14 mL). This was heated for 4 h 30 min at 150 °C in the microwave. NMR analysis of a reaction aliquot was done. **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 8.62 – 8.40 (m, 1H), 7.75 – 7.62 (m, 1H), 7.52 – 7.29 (m, 4H), 7.29 – 7.09 (m, 3H), 6.91 – 6.84 (m, 1H), 4.07 (d, *J* = 4.3 Hz, 1H), 3.79 (dt, *J* = 16.1, 6.6 Hz, 2H), 1.55 (s, 4H), 1.60 – 1.44 (m, 3H), 1.47 – 1.19 (m, 19H), 0.88 (tq, *J* = 7.1, 4.8 Hz, 16H), 0.85 – 0.67 (m, 2H); **$^{11}$B NMR** NMR (128 MHz, CHLOROFORM-D) δ 31.49, 17.34 – -11.99 (m), -1.88; **$^{19}$F NMR** NMR (376 MHz, CHLOROFORM-D) δ -89.63, -133.16, -142.36 (dd, *J* = 37.7, 17.8 Hz), -148.33 – -151.61 (m), -154.12.

After adding 0.5 mL of water and another 1.5 h in the microwave a column was done (4:1, cyclohexane:acetone). Another NMR analysis was done. Cinnamaldehyde: **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 9.67 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.51 – 7.31 (m, 5H), 7.22 – 7.11 (m, 0H), 6.69 (dd, *J* = 15.9, 7.7 Hz, 1H), 1.40 (s, 1H). Butyl compound: **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 4.34 (s, 0H),

2.16 (s, 0H), 1.61 – 1.51 (m, 0H), 1.43 (s, 0H), 1.41 – 1.22 (m, 3H), 0.89 (q, *J* = 7.1 Hz, 6H); **$^{11}$B NMR** NMR (128 MHz, CHLOROFORM-D) δ 32.18.

Failed synthesis

## 5.12 Allyl transfer mimicking May et.al.



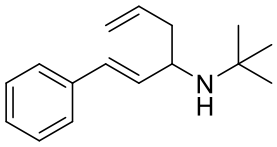

**3c** **14c** **35**

A microwave reaction tube was charged with 4 Å powdered molecular sieves (1.25 g), *trans*-cinnamaldehyde (1 mmol, 0.13 mL), potassium allyltrifluoroborate (3 eq., 0.444 g) and toluene (3 mL). This was heated for 6 h at 125 °C in the microwave. An NMR analysis of a reaction aliquot was done.

**$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 7.43 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.36 (s, 30H), 7.34 – 7.20 (m, 14H), 7.19 (q, *J* = 5.8 Hz, 9H), 7.12 (d, *J* = 1.5 Hz, 1H), 6.74 (dd, *J* = 15.7, 10.3 Hz, 1H), 6.48 (td, *J* = 19.0, 8.0 Hz, 3H), 6.40 – 6.29 (m, 1H), 6.08 – 6.00 (m, 1H), 5.85 – 5.77 (m, 2H), 3.59 (dd, *J* = 13.1, 9.7 Hz, 1H), 3.34 (s, 1H), 2.71 (d, *J* = 13.9 Hz, 1H), 2.43 – 2.29 (m, 4H), 2.06 – 1.95 (m, 2H), 1.76 (s, 3H), 1.42 – 1.30 (m, 1H), 1.24 (d, *J* = 2.7 Hz, 1H).

The filtration solid got washed with MeOH and an NMR analysis of that was done also. Allyltrifluoroborate: **$^{1}$H NMR** (400 MHz, ACETONITRILE-D3) δ 5.88 (dq, *J* = 17.1, 8.4 Hz, 1H), 4.69 – 4.60 (m, 1H), 4.60 – 4.53 (m, 1H), 2.15 (s, 2H), 1.01 (s, 2H).; **$^{11}$B NMR** (128 MHz, ACETONITRILE-D3) δ 3.23 (q, *J* = 61.0 Hz); **$^{19}$F NMR** (376 MHz, ACETONITRILE-D3) δ -140.43 (dd, *J* = 119.7, 57.1 Hz).

## 5.13 (*E*)-N-(tert-butyl)-1-phenylhexa-1,5-dien-3-amine (36)




**36**

A microwave reaction tube was charged with potassium allyltrifluoroborate (1 eq., 0.296 g), cinnamaldehyde *tert*-butylimine (2 mmol, 0.374 g), toluene (4 mL) and $BF_3OEt_2$ (1 eq., 0.25 mL) This was heated for 1 h 45 min at 150 °C in the microwave. The reaction got filtered through a fritted funnel and the solvent got removed under reduced pressure. For purification of the product two columns were done (4:1 and 6:1, hexane:ethylacetate). An NMR analysis of the product was done. **Yield**: 19 %; **$^{1}$H NMR** (400 MHz, CHLOROFORM-D) δ 7.40 – 7.32 (m, 2H), 7.35 – 7.15 (m, 4H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.9, 8.0 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.1, 7.2 Hz, 1H), 5.15 – 5.04 (m, 2H), 3.48 (q, *J* = 7.2 Hz, 1H), 2.33 – 2.25 (m, 2H), 1.30 – 1.17 (m, 2H), 1.12 (s, 8H), 0.92 – 0.79 (m, 1H), 0.82 (s, 1H).

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