TECHNISCHE UNIVERSITÄT WIEN
Vienna University of Technology

Diplomarbeit

Selective Hydroboration of Terminal Alkenes using Well-defined Mn(I) Complexes

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines

Diplom-Ingenieurs

unter der Leitung von

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und

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Wien, im August 2020 _____

Ich habe zur Kenntnis genommen, dass ich zur Drucklegung meiner Arbeit unter der Bezeichnung

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Wien, im August 2020 _____

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Danksagung

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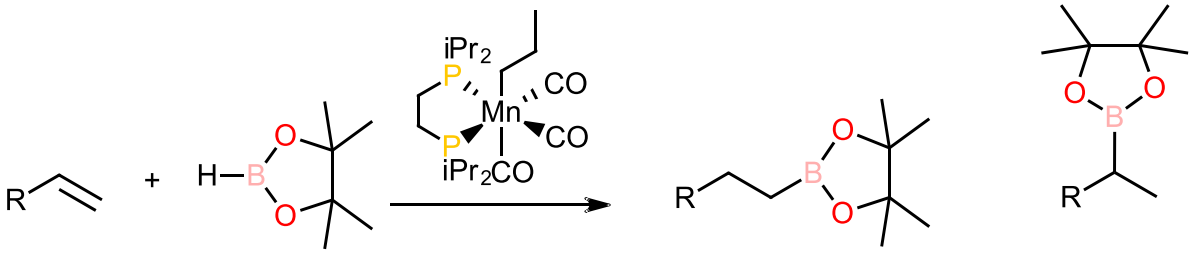
Abstract

This thesis is dedicated to the utilisation of a well-defined manganese(I) complex for hydroboration reactions of terminal alkenes.

The first step was to finely tune the reaction conditions as to achieve full conversion. This was done by changing different parameters of the reaction such as the solvent, temperature, reaction time and the amount of the starting materials. During this optimisation procedure, the catalyst loading could be decreased to 0.25 mol%.



R = alkyl or aryl

anti-Markovnikov (linear)

Markovnikov (branched)

Next step was to come up with a quick and easy work-up which could be applied to all conducted catalysis reactions. Due to optimisation of the work-up procedure, column chromatography could be omitted during the purification process.

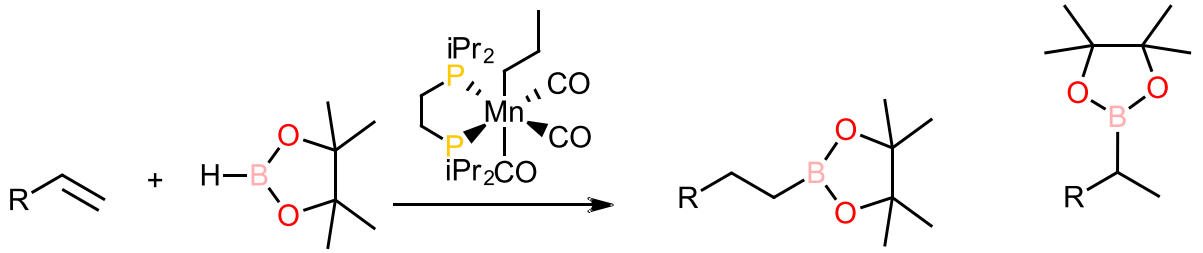
Last step was to hydroborate a broad range of different alkenes to determine the scope and limitation. High reactivity could be achieved for aromatic as well as aliphatic systems.

The implemented catalytic protocol showed high functional group tolerance, as halides, ether, amines and esters were well-tolerated.

Kurzfassung

Diese Arbeit befasst sich mit der Hydroborierung von terminalen Alkenen mittels eines definierten Mangan(I) Komplexes.

Im ersten Schritt wurden die Reaktionsbedingungen solange angepasst, bis ein vollständiger Umsatz erreicht wurde. Dies geschah durch die Änderung verschiedener Parameter wie der Temperatur, Reaktionszeit und der Stoffmengen der eingesetzten Edukte. Dabei konnte die benötigte Menge an Katalysator auf 0.25 mol% reduziert werden.



R = Alkyl oder Aryl

anti-Markovnikov (linear)

Markovnikov (verzweigt)

Im nächsten Schritt wurde eine schnelle und einfache Aufarbeitung ausgearbeitet, welche für alle durchgeführten Katalysen eingesetzt werden konnte. Aufgrund der Optimierungen konnte auf Säulenchromatographie während der Aufarbeitung verzichtet werden.

Im letzten Schritt wurde eine Reihe von Alkenen hydroboriert, um die Toleranz gegenüber anderen funktionellen Gruppen und Anwendungsbereich des Katalysators zu untersuchen. Es konnten hohe Reaktivitäten sowohl für aromatische als auch für aliphatische Systeme erzielt werden.

Das implementierte katalytische System zeigte eine hohe Toleranz gegenüber funktionellen Gruppen wie Halogeniden, Ethern, Aminen und Estern.

1 Introduction

Chemical processes are at the basis of most of the products we use every day. May it be fertiliser for growing plants, pharmaceuticals to cure one's illnesses or the plastic we use in most of our daily appliances.[1] Most of these chemical processes, however, have quite unfavourable kinetics on their own, which means that most starting materials would decompose before the reaction would occur. The main reason is the activation energy which needs to be reached for any reaction to happen.[2]

One major strategy to circumvent this problem is the utilisation of a catalyst. Basically, catalysts reduce the activation energy needed for a specific reaction, making it much more feasible, as can be seen in Figure 1. During catalysis the catalyst is not consumed and thus can repeat the catalytic process.[1]

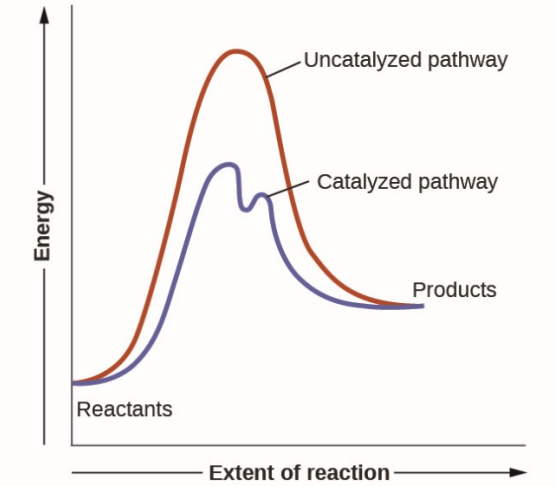


Figure 1 - Activation energy with and without catalyst[3]

Most catalysts must be tailored to the specific reaction. In general, there are two different types of catalysis: homogeneous and heterogeneous.

Heterogenous catalysis takes place on the interface between two phases with the catalyst being in a different phase than the reactants. Thus, the catalyst can relatively easily be removed from the products, resulting in a high regeneration thereof. Disadvantage of heterogeneous catalysis include the lower reactivity, leading to harsh reaction conditions due to limited surface area of the catalyst and often a lack of chemoselectivity.

In homogeneous catalysis all reactants and the catalyst are in the same phase where the reaction takes place. This removes the limitations of heterogeneous catalysis as there is no

limited interface and by tuning the electronic and steric features of the catalyst, high chemoselectivity can be achieved. However, the catalyst is often much harder to remove or regenerate.[1]

A multitude of different substances can act as catalysts. In Nature enzymes can most prominently be found, which act as catalysts in all biological systems. They also catalyse reactions in bioreactors which have become increasingly important in the synthesis of pharmaceuticals.[4] There are also organic substances that can act as catalysts, for example L-proline.[1] Additionally, metal-based systems are widely utilised catalysts in organic synthesis.

These catalysts can most often be encountered in the form of metal complexes which consist of a central metal atom and different ligands that are bound to the metal. Titanium, Cobalt, Rhodium and Palladium are among the most frequent central atoms as they have proven to be able to catalyse a broad range of different organic reactions. Ligand architecture is also highly varied as there are countless ligands that can be utilised, including chelating ligands which bind to the metal centre multiple times. This high variance has resulted in a high number of different metal-based catalysts and the ongoing improvement thereof.[5] Some example for prominent metal-based catalysts are shown below in Figure 2.[6,7]

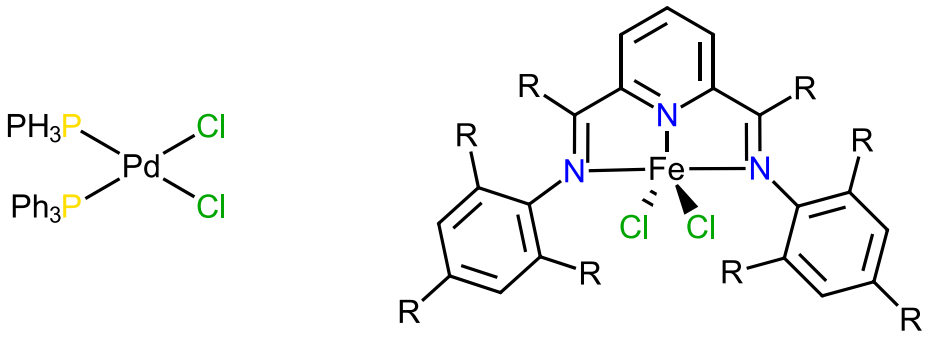


Figure 2 - Prominent metal-based catalysts

1.1 Hydroboration

Hydroborations of unsaturated compounds are among the most important reactions in modern organic chemistry. Boranes are often used in organic synthesis as platform chemicals for a wide variety of different synthetic routes. Oxidation, amination, halogenation, cross-coupling and carbonylation are some example for possible reactions of organoboranes, as shown in Figure 3.[8]

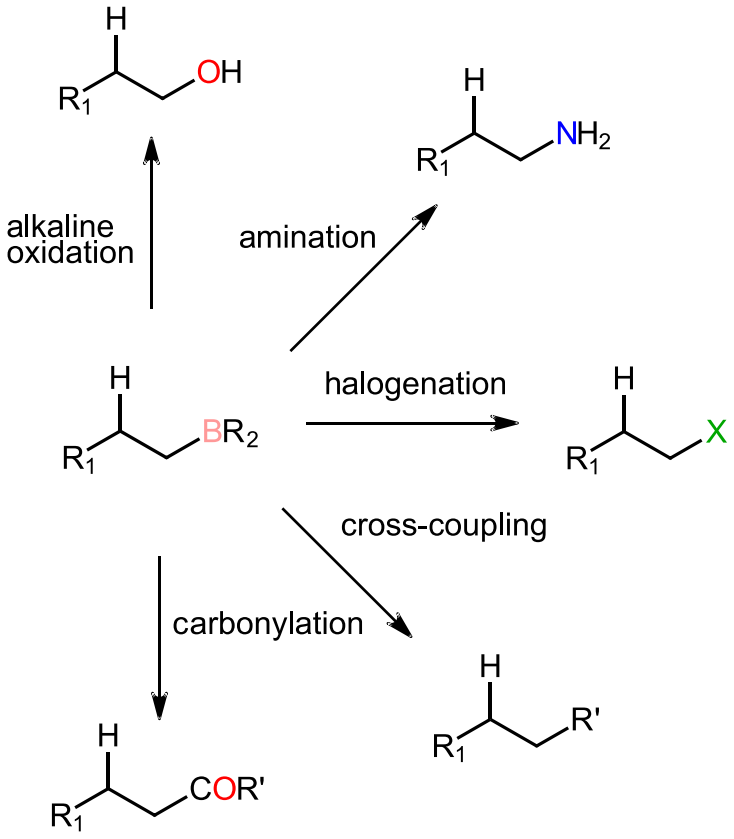


Figure 3 - Further reactions of organoboranes

Hydroboration is the reaction of an unsaturated system such as a double or triple bond with a borane such as BH_3, resulting in the addition of a hydrogen and a borane (Figure 4).[8]

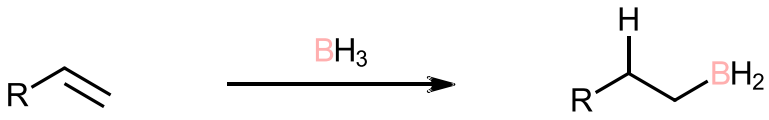


Figure 4 – Hydroboration of an alkene with monoborane

With highly reactive boranes such as BH_3 the reaction occurs spontaneously, but rigorous safety measurements must be taken as it reacts violently with oxygen and water. This aspect

has driven the search for more stable boranes that could be handled more easily. Frequently used boranes are depicted in Figure 5.

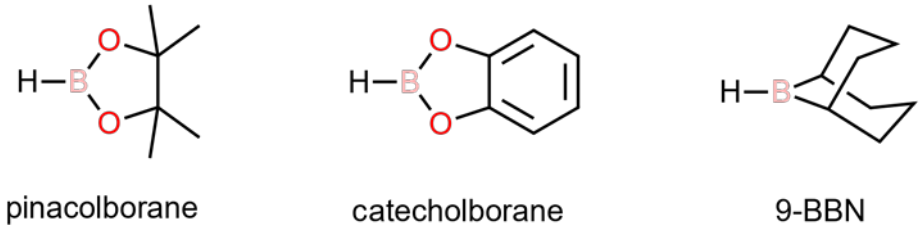


Figure 5 – Prominent boranes in hydroboration reactions

As the reactivity of these boranes is significantly lower than that of BH_3, they do not react with an unsaturated system spontaneously in good yields. For that purpose, catalysts were ought to be researched to catalyse these types of reactions.[9]

One of the first metal complexes used for hydroboration of alkenes and alkynes was the Wilkinson Catalyst, as seen in Figure 6.[10]

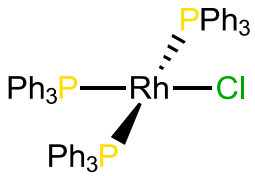


Figure 6 – Wilkinson catalyst

Since then, numerous research groups have synthesised complexes that are able to catalyse hydroboration reactions with unsaturated carbon-carbon bonds. Despite extensive investigations, there is still no generally accepted mechanism for this reaction and varies highly depending on the catalyst.[9]

There is also a high degree of variation in the chemoselectivity, regioselectivity and, if applicable, enantioselectivity of these catalytic systems. These factors are highly dependent on the central metal, ligands and the substrates themselves.

Initially, most research focused on the use of precious metals as they were well researched in other types of catalysis such as carbon-carbon coupling. Nonetheless, the use of nonprecious transition metals has increased recently to provide cheaper and more accessible catalysts. Furthermore, there are a few examples for the use of main group compounds that can be used for specific hydroboration reactions. Some examples were demonstrated by Hill et al. and Kinjo et al. for the utilisation in the hydroboration of aldehydes and ketones (Figure 7).[11,12]

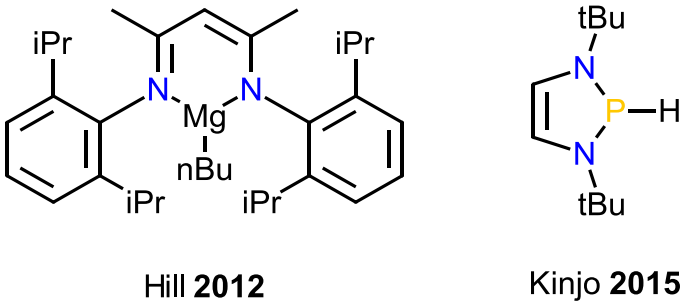


Figure 7 - Main group compounds for hydroboration of aldehydes and ketones

In the case of alkenes, the anti-Markovnikov product is usually formed when reacting with BH_3. This is due to the BH_3 adding in *cis*-position and the BH_2 moiety preferring the less sterically hindered carbon. Nonetheless, there are examples for Markovnikov products as for example from Aggarwal et al., using a Rh catalyst.[13] A reaction scheme with pinacolborane is depicted in Figure 8.

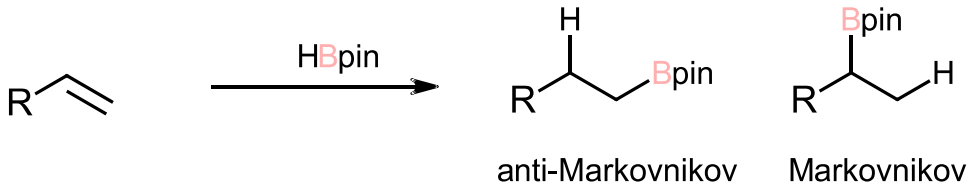


Figure 8 - Hydroboration with pinacolborane

In the case of alkynes, the *cis* product is most often formed, but there are some examples for the formation of the *trans* product as shown by Miyaura et al. who used Rh and Ir catalysts in combination with triethylamine.[14]

In addition to alkenes and alkynes, unsaturated carbon-oxygen and carbon-nitrogen bonds like ketones, aldehydes, amides, imines and nitriles may also be hydroborated. Comparatively, this is a more recent research topic and is especially useful in the synthesis of alcohols. As most hydroboration can be done under very mild conditions, carbonyl compounds can easily be hydroborated and hydrolysed to afford alcohols.[9]

One of the most promising hydroboration reactions is reduction of CO_2. Carbon dioxide is a prominent greenhouse gas and can serve as an inexpensive carbon source that can easily be handled as it is nonflammable and nontoxic. This reaction can thus provide a multitude of different important bulk chemicals like formic acid, formaldehyde, methanol and even methane.[9] One of the first transition metal catalysed hydroboration reactions of CO_2 was

reported by Nozaki et al. who used a Cu(I) carbene complex in combination with pinacolborane.[15]

1.1.1 Precious Metals in Alkene Hydroboration

Following the discovery of the first metal based catalyst for hydroboration of alkenes based on Rh in 1975, precious metal catalysis was at the forefront of research.[10] Numerous catalysts with precious metals have been developed since then, mostly with Rh, Ir and Cu as the central atoms.[16,17]

The catalytic cycles of each catalyst vary to a certain degree, however, there is a general proposed catalytic cycle, that depicts the essential steps in most precious metal-based alkene hydroboration reactions. It is shown in Figure 9.[9]

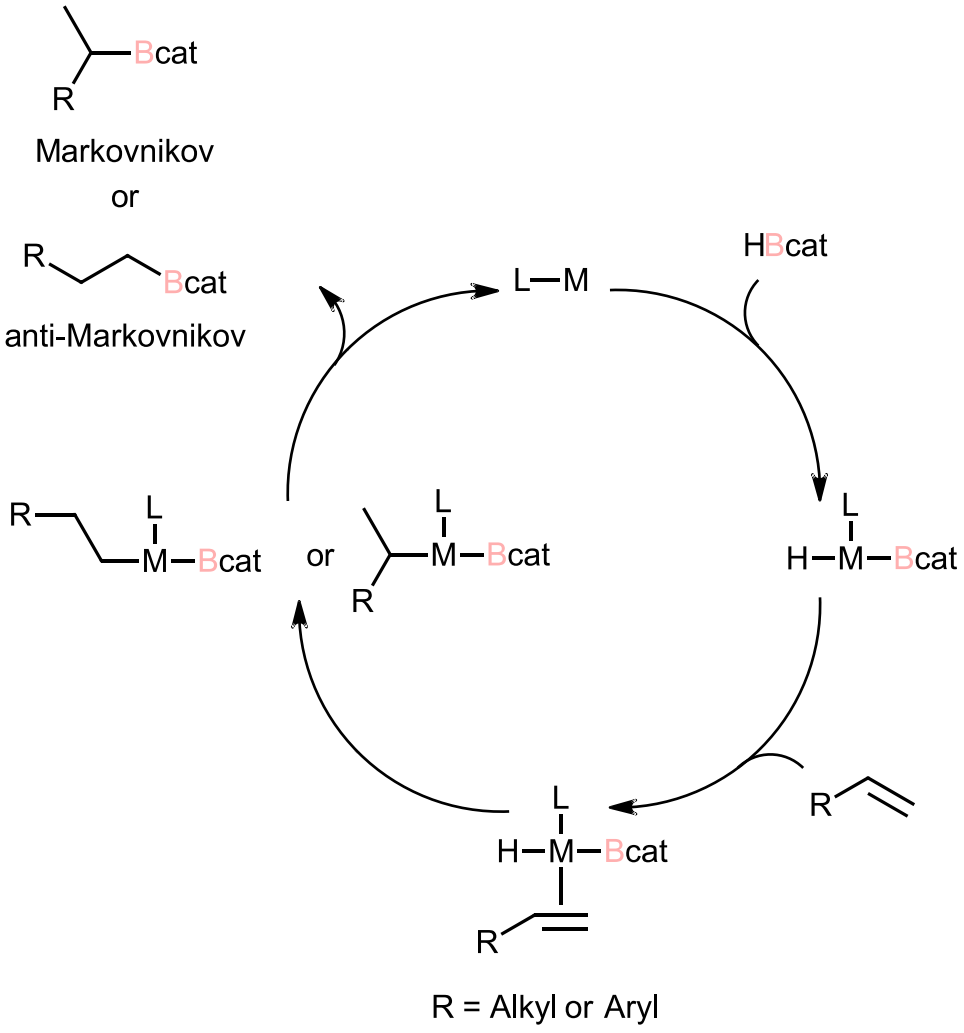
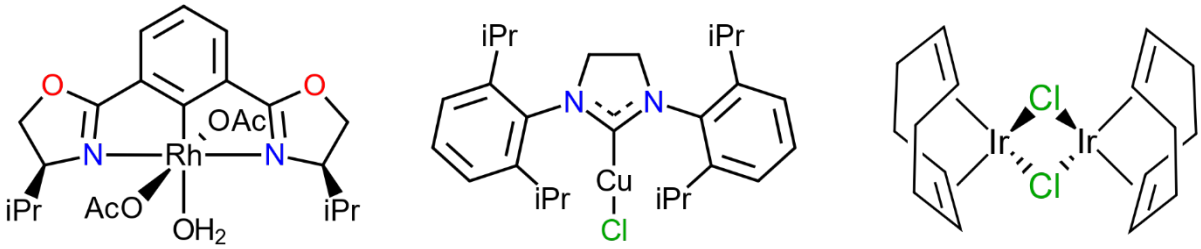


Figure 9 - Proposed catalytic cycle for precious metals

The first step is an oxidative addition of the borane to the metal complex. Then the alkene coordinates to the complex *via* π-binding after which it inserts into the metal-hydrogen bond. The last step is a reductive elimination, cleaving the hydroborated alkene and reforming the catalytically active species.[17]

In Figure 10 several precious metal catalysts for hydroboration reactions are shown.[13,18,19]



Aggarwal **2017** | Montgomery **2016** | Miyaura **2004**

1 | **2** | **3**

Figure 10 - Precious metal catalysts for alkene hydroboration

Catalyst **1** is notable as it affords the asymmetric Markovnikov product. This is achieved by using a mixed sp^2-sp^3 diboron species, depicted in Figure 11, that must be synthesised beforehand. As one boron atom is coordinatively saturated it can be protodemetalated in a following step, affording the desired Markovnikov hydroborated species. However, in addition to 5 mol% of catalyst **1**, water as a proton source and catalytic amounts of sodium *tert*-butoxide are needed.[13]

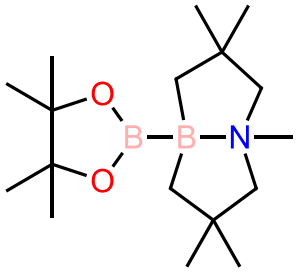


Figure 11 - Mixed diboron species

Catalyst **2** was one of the first metal complexes that was able to afford the Markovnikov product. This is mainly due to the steric hinderance brought by the *iso*-propyl groups that leads to the branched isomer.[18] Catalyst **3** affords the anti-Markovnikov product but requires the addition 2 eq. of 1,1-bis(diphenylphosphino) methane to be catalytically active.

1.1.2 Base Metals in Alkene Hydroboration

In addition to precious metals, base metals can also be utilised for alkene hydroboration. This field of study has seen a strong rise in popularity in the last few years as base metals are comparably cheap, generally have a low toxicity and are more sustainable. Unfortunately, application of base metals has its challenges: They often undergo single electron transfer processes which makes them very prone to exhibiting unwanted side reactions. Therefore, ligand architecture must be finely tuned in order to suppress these reactions.[20]

Compared to precious metals, there is also a higher variance in reaction mechanisms between catalysts. There is a general proposed catalytic cycle (Figure 12), but it is only applicable to certain catalysts.

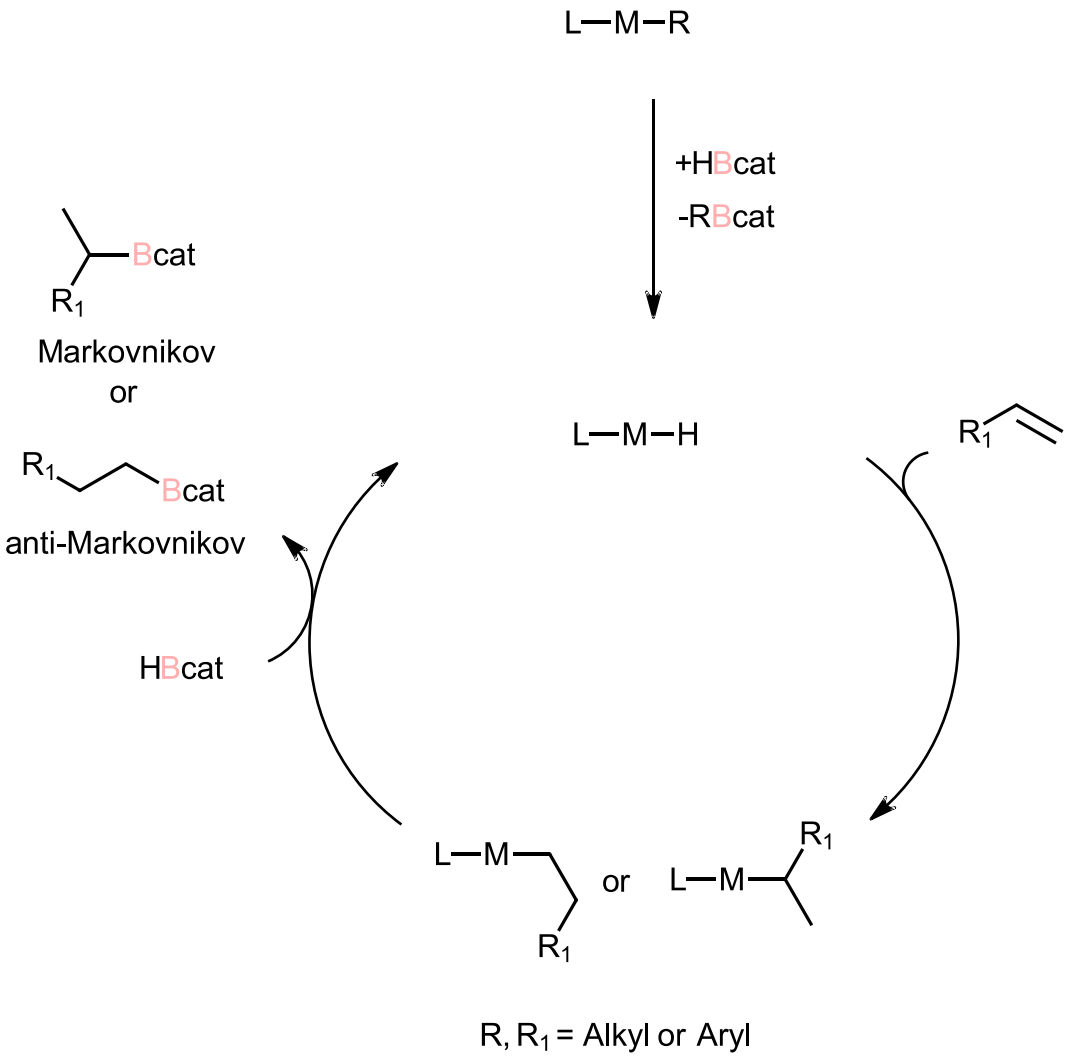


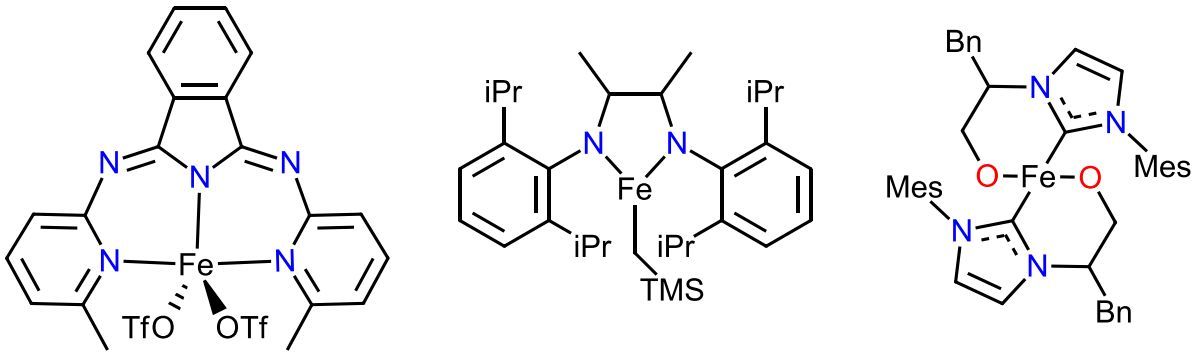
Figure 12 - Proposed catalytic cycle for base metals

Instead of an oxidative addition and reductive elimination step, the double bond inserts directly into the metal-hydrogen bond, after which the hydroborated species is cleaved.[21]

Base metals such as iron, cobalt and nickel have been extensively researched for the use in catalysis. There is a wide variety of complexes already known to catalyse an increasing number of reactions that were only possible with precious metals before.[20] In addition to that, manganese has also seen an increase in interest as a catalyst in hydroboration reactions.[22–24]

Numerous different iron-based catalyst for the hydroboration of alkenes exist, some examples are shown in Figure 13.

A high catalyst loading of around 2.5 – 5 mol% is often needed and sometimes a reductant must be employed. However, the reactions can very often be done at ambient temperature, which is very advantageous when working with unstable chemicals. Hereby catalyst **4** and **5** afford the anti-Markovnikov product, catalyst **6** the Markovnikov one.[25–27]

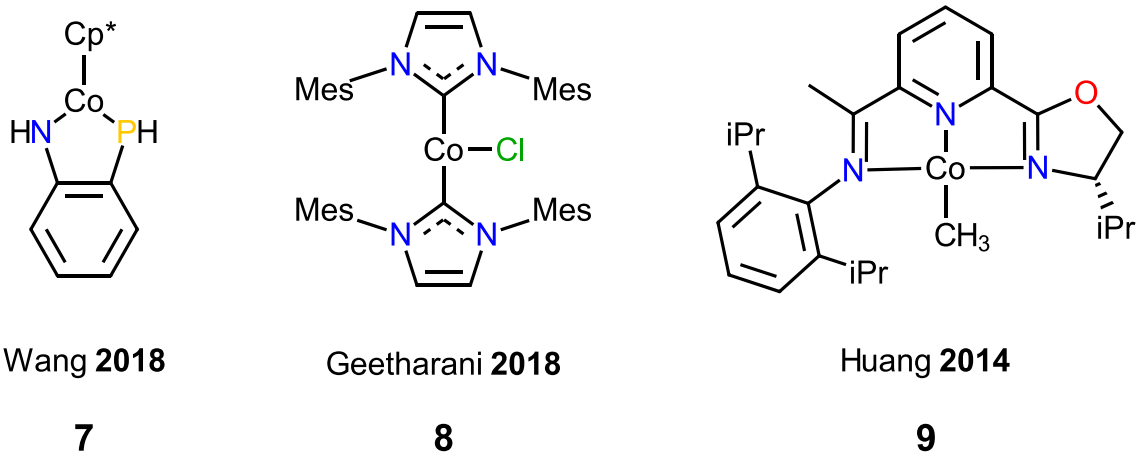


Szymczak **2015** | Webster **2016** | Thomas **2016**

4 | **5** | **6**

Figure 13 - Iron-based catalysts for alkene hydroboration

There are numerous examples for cobalt-based catalysts in hydroboration, as shown in Figure 14. Most operate at comparatively low catalyst loadings of around 0.5 - 3 mol% and mild temperatures of around 25 - 50°C. Additionally, reductants as activators are rarely needed.



Wang **2018** — **7**

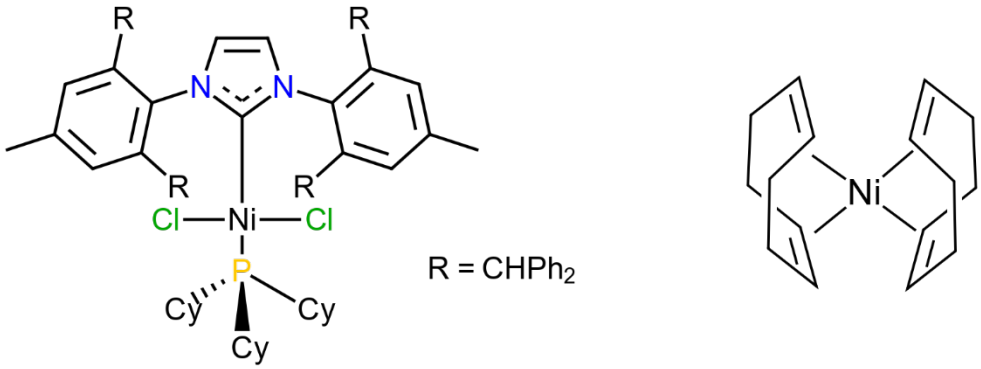
Geetharani **2018** — **8**

Huang **2014** — **9**

Figure 14 - Cobalt-based catalysts for alkene hydroboration

Catalyst **7** can perform an isomerisation hydroboration, in which the double bond migrates from an internal to a terminal position, after which it is hydroborated. Catalysts **8** and **9** are also notable for their Markovnikov- and enantioselectivity, respectively.[28–30]

Compared to Co, there are only a few Ni-based systems for alkene hydroboration, some examples are shown in Figure 15. They often need quite high catalyst loadings and a reductant.



Schomaker **2016** — **10**

Wang **2017** — **11**

Figure 15 - Nickel-based catalysts for alkene hydroboration

Catalyst **10** for example is able to afford the Markovnikov product for a limited number of styrene derivatives. However, 6 mol% of potassium *tert*-butoxide are additionally needed. Catalyst **11** operates without a base and at comparatively low catalyst loadings of 2 mol%, but addition of 4 mol% of tri-*tert*-butylphosphine as ligand is mandatory.[31,32]

1.2 Manganese in organic synthesis

In addition to cobalt, iron and nickel, manganese has seen a strong rise in interest as a base-metal catalyst in the last decade. Contrary to cobalt and nickel, manganese is non-toxic and environmentally benign, in addition to being very abundant and thus cheap to acquire.

Manganese has a very high number of possible oxidation states, namely between -III to +VII, and can have a coordination number of up to 7. This makes it very diverse as a lot of different compounds can be synthesised with manganese. One notable example is $KMnO_4$ which is a strong oxidising agent.[33]

There are several reactions that can potentially be catalysed by manganese complexes. First examples were the epoxidation of alkenes and oxidative free-radical cyclisation catalysed with manganese(III) acetate.[34] More recently reported reactions include hydrogenation, hydrofunctionalisations such as hydrosilylation and hydroboration, cross-coupling and C-H activation.[33]

1.2.1 Hydrogenation and Dehydrogenation

There are numerous catalytic systems based on manganese that can hydrogenate a wide variety of different functional groups. Very similar to hydroboration, C=O and unsaturated C-C and C-N bonds can be hydrogenated. Mostly used for that application are pincer-type ligands of the type PNP and PNN, although there are examples of complexes with bidentate ligands.[35,36] As hydrogen source can either serve hydrogen gas or an added compound that may also serve as the solvent, for example alcohols.[37]

There is a wide variety of manganese-based catalysts for hydrogenation of carbonyl compounds, some are shown in Figure 16.

Catalyst **12** is noteworthy as it features a bidentate NHC-phosphine ligand instead of a pincer-type ligand. It can be employed to hydrogenate a variety of ketones to alcohols and is catalytically active at low catalyst loadings of 0.1 mol%. However, in addition to the catalyst, either 1 mol% of sodium *tert*-butoxide or KHMDS as base are needed.[36]

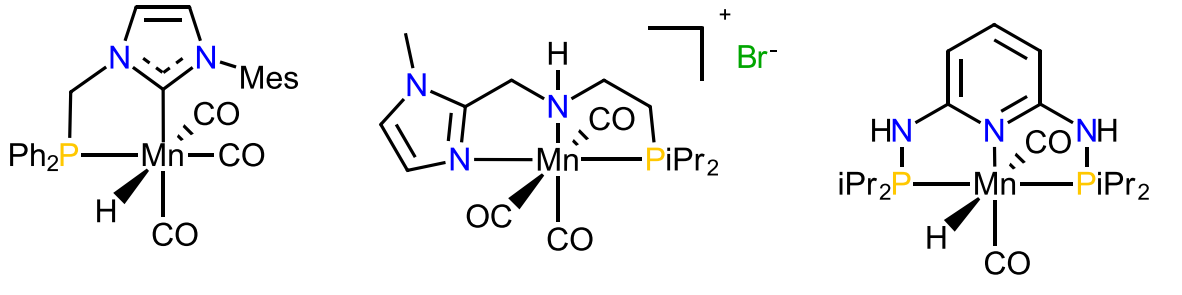


Figure 16 - Manganese-based catalysts for hydrogenation of carbonyl compounds

Catalyst **13** on the other hand features a PNN pincer-type ligand and is used for the hydrogenation of amides. Quite high catalyst loadings between 2-5 mol% are needed, and it can be used on primary, secondary and tertiary amides. This reaction yields an alcohol and the corresponding amine, a reaction scheme can be seen in Figure 17.[38]

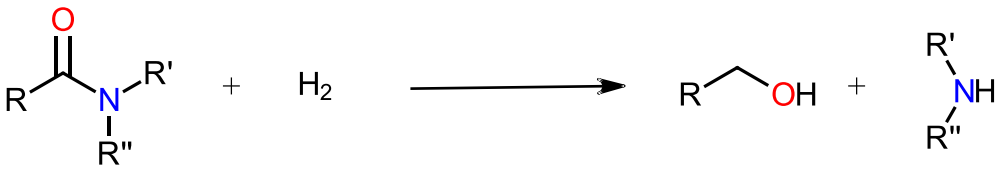
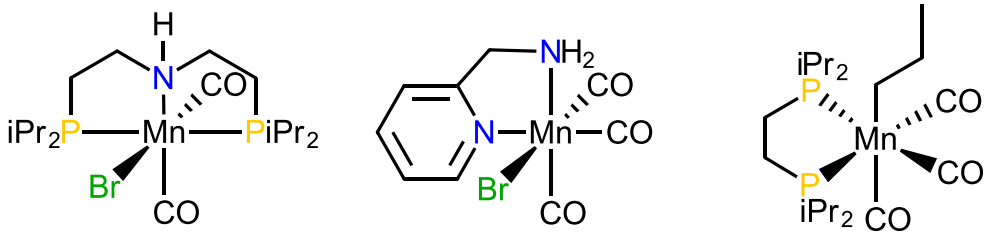


Figure 17 - Hydrogenation of amides

Catalyst **14** is used for the hydrogenation of carbon dioxide to form formic acid. It requires DBU as a base and LiOTf as a lewis acid and can achieve very high turnover numbers of up to 30 000.[39]

In Figure 18, various catalysts for the (transfer)hydrogenation of unsaturated C-N or C-C bonds are shown. Catalyst **15** is utilised for the hydrogenation of various nitriles, yielding primary amines. 50 bar H_2 pressure, 10 mol% sodium *tert*-butoxide and a temperature of 120°C are needed, with a reaction time between 24-60 hours, depending on the substrate.[40]



Beller **2016** Sortais **2019** Kirchner **2019**

15 **16** **17**

Figure 18 - Manganese based catalysts for hydrogenation of nitriles, imines and alkenes

Catalyst **16** is able to reduce a wide variety of aldimines with isopropanol as hydrogen source after activation with a base. Noteworthy is the short reaction time of only 3 hours.[41] Catalyst **17** on the other hand can hydrogenate mono- and disubstituted alkenes and does not need any further additives. Less sterically hindered alkenes can be hydrogenated at 25°C, whereas 1,2-disubstituted alkenes require 60°C.[42]

Dehydrogenation reactions can also be catalysed with well-defined manganese(I) complexes. It is the reverse reaction of hydrogenation and can thus be most prominently used for the formation of ketones and aldehydes from alcohols. This opens up a wide variety of different reactions with a dehydrogenative pathway like the coupling of amines with alcohols or the condensation of an alcohol and a nitrile.[43]

1.2.2 Hydrosilylation of unsaturated compounds

Hydrosilylation is an important reaction for the chemical industry and formed products cannot only be reacted further, but also be used as emulsifiers, adhesives and softeners, to

name a few. There are two main groups of bonds that can be hydrosilylated: carbonyls and unsaturated C-C bonds.[44]

There are quite a few manganese-based catalysts known for the hydrosilylation of carbonyl compounds, some notable examples are shown in Figure 19.

Catalyst **18** utilises $PhSiH_3$ to convert a wide variety of ketones into alcohols. It operates with catalyst loadings of 0.5 mol% and only 0.5 equivalents of silane must be added. Especially notable is the oxidation state of manganese of +V in this complex.[45]

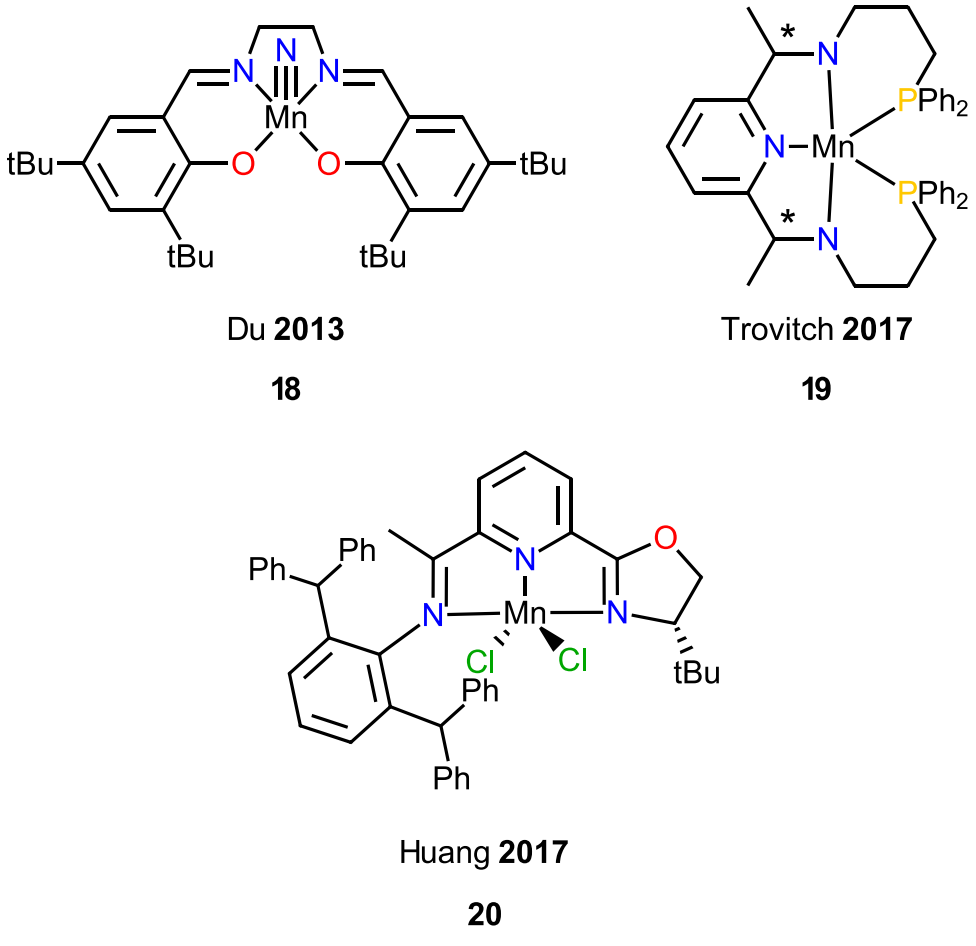


Figure 19 - Manganese-based catalysts for hydrosilylation of carbonyl compounds

Catalyst **19** hydrosilylates aldehydes, also utilises $PhSiH_3$ and operates at very low catalyst loadings of only 0.1 – 0.01 mol%. It is catalytically active at room temperature and the reaction

time needed is only 2 minutes. To afford the alcohol, however, the product must be reacted with aqueous NaOH for 2 hours afterwards. A reaction scheme is depicted in Figure 20.

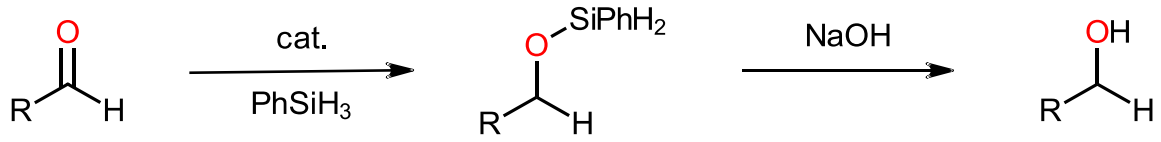


Figure 20 - Hydrosilylation of aldehydes and subsequent reaction with NaOH

In addition to hydrosilylation, dihydrosilylation is also possible with this catalyst.[46] Catalyst **20** is remarkable as asymmetrical hydrosilylation of aryl ketones is possible after activation with a base.[47]

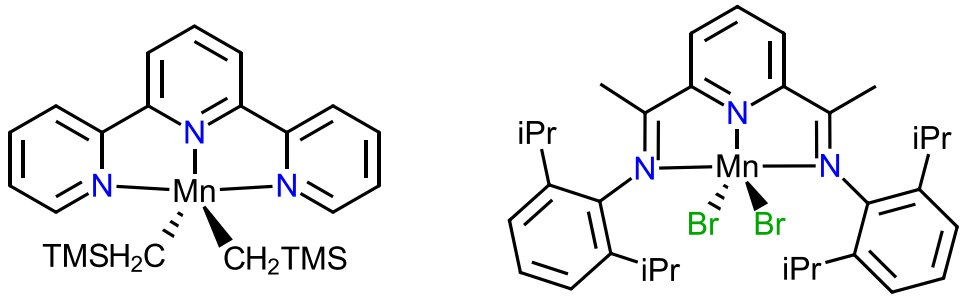
Compared to the reaction with C=O compounds, there are even fewer examples for the hydrosilylation of unsaturated C-C bonds. One reason is the much lower polarity of the bond and its tendency to undergo side reactions.[44]

An example is given for the hydrosilylation of alkynes: either 5 mol% of $Mn(CO)_5Br$ with 20 mol% of triphenylarsine or 10 mol% of $Mn_2(CO)_{10}$ with 20 mol% lauroyl peroxide is used to form the *E* or *Z* isomer, respectively. A temperature of 120 – 150°C is needed, achieving good to excellent enantioselectivity.[48] Alternatively, $Mn_2(CO)_{10}$ in combination with blue LED light may be employed, forming the *Z*-isomer.[49]

1.2.3 Hydroboration

So far, there are only two manganese-based catalysts for the hydroboration of alkenes, one affording the branched, one affording the linear product. Both catalysts consist of a manganese in the oxidation state +II as the central atom and feature NNN-pincer type ligands.

The first reported manganese-based catalyst for alkene hydroboration is shown in Figure 21. Catalyst **21** yields the Markovnikov product with pinacolborane, operates at a low catalyst loading of 1 mol%, and at a temperature of 25°C. The highest conversions can be achieved with styrene derivatives, but a limited number of other alkenes can also be hydroborated. No further reductants or bases are needed. In addition to that, hydroboration of ketones and aldehydes is possible at the same catalyst loading. If an unsaturated aldehyde or ketone is used, the carbonyl moiety is chemoselectively hydroborated.[22]



Zheng **2016** Thomas **2018**

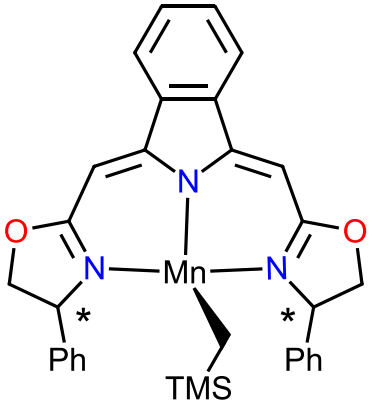
21 **22**

Figure 21 - Manganese-based catalysts for alkene hydroboration

The second manganese-based catalyst used for the hydroboration of alkenes is also shown in Figure 21. It can be used on a variety of different styrene and some linear alkene derivatives.

In addition to 2 mol% of catalyst **22**, 6 mol% sodium *tert*-butoxide must be added for the catalysis to work. In contrast to the catalyst mentioned before, it forms mostly the linear product. Electron-withdrawing substituents on the phenyl ring like trifluoromethyl or bromide lead to lower yields, electron-donating groups like *tert*-butyl to higher yields. Hydrosilylation of alkenes is also possible with this catalyst.[50]

A manganese-based catalyst for the hydroboration of ketones is depicted in Figure 22. 2.5 mol% of catalyst **23** in toluene at comparably low temperatures of -40°C to 25°C were used without any further additives. When using the *S* enantiomer of the ligand, it mostly affords the *S* enantiomer of the product, achieving good to excellent stereoselectivity on most substrates.[23]

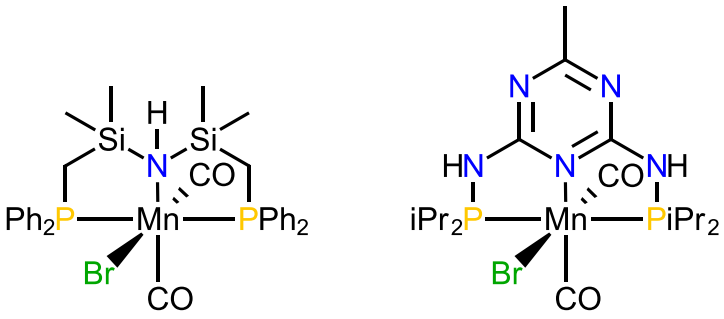


Gade **2017**

23

Figure 22 - Manganese-based catalyst for ketone hydroboration

Apart from alkenes and ketones, other functional groups can be hydroborated with manganese-based catalysts. Two such catalysts are shown above in Figure 23, both featuring PNP pincer type ligands and manganese in oxidation state of +I. Catalyst **24** has been shown to hydroborate carboxylic acid, carbonates and carbon dioxide. The temperature needed ranges between 80 to 120°C and the catalyst loading between 0.1 - 0.2 mol%. However, a base is needed to achieve good yields, such as potassium *tert*-butoxide or triethylamine.[24]



Leitner **2018** Maji **2019**

24 **25**

Figure 23 - Manganese-based catalyst for carboxylic acid hydroboration

Catalyst **25** in contrast is only able to hydroborate carboxylic acids but does not need a base and achieves almost full conversion on a broad range of substrates at 0.1 mol%.[51]

The reaction for carboxylic acids is shown in Figure 24, it follows a deoxygenative pathway and affords an alkyl boronate ester which can then be converted to an alcohol. It thus serves as an alternative to the reduction with $LiAlH_4$ or $NaBH_4$.[52]

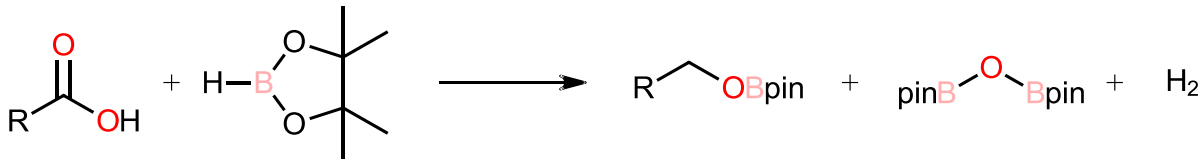
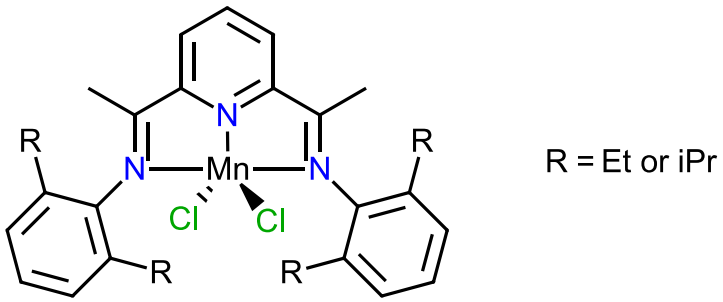


Figure 24 - Reaction mechanism of deoxygenative hydroboration

In addition to the hydroborated product, a diboryl ether is formed, therefore requiring at least 3 equivalents of pinacolborane. The reaction with carbonates and carbon dioxide also follows this reaction pathway.[24]

Internal alkynes can also be hydroborated with catalysts as shown in Figure 25, as demonstrated with the hydroboration of a variety of propargylic alcohols and amines.



Rueping **2020**

26

Figure 25 - Manganese-based catalyst for alkyne hydroboration

For that purpose, a catalyst loading between 2 – 10 mol%, 4 – 20 mol% $NaBHEt_3$ and the catalyst **26** bearing the *iso*-propyl groups is needed. Before starting the reaction, however, the alcohol and the amine had to be protected. Symmetric internal alkynes were also reacted with the catalyst **26** bearing ethyl groups under the same conditions, resulting in good to excellent conversions.[53]

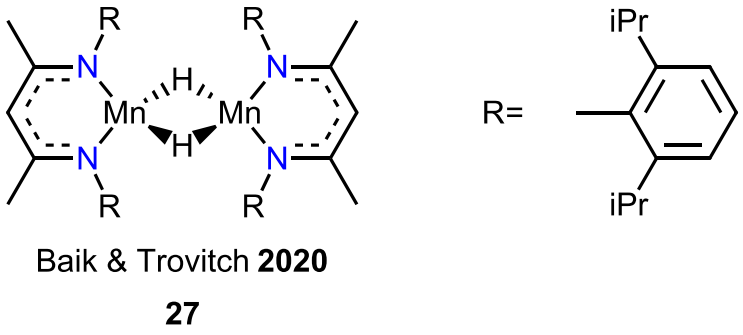


Figure 26 - Manganese-based catalyst for dihydroboration of nitriles

Recently discovered is the dihydroboration of nitriles with a manganese hydride dimer (Figure 26), a reaction scheme is shown in Figure 27.

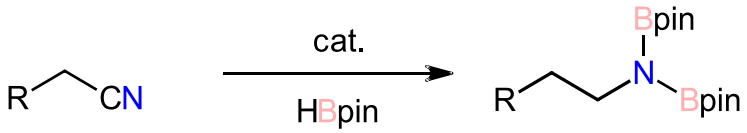


Figure 27 - Dihydroboration of nitriles

It is able to afford N,N-diborylamines, achieving good to excellent yields at a catalyst loading of 0.5 mol% (1 mol% Mn) without any additives.[54]

1.2.4 Cross-coupling

The catalytic formation of C-C bonds is of great importance in organic chemistry. In most cases, palladium is used and well established for a multitude of different cross-coupling reaction.[55] Manganese can also be utilised for these kinds of reactions and there are a few examples of such systems.[33] One example is the utilisation in Stille cross-coupling, where 10 mol% $MnBr_2$ was used in combination with 1 eq. NaCl to react aryl- or alkynyl-iodine reagents with different stannanes. This reaction, however, needed quite high temperatures of 120°C.[56] The reaction of aryl chlorides with Grignard reagents catalysed by $MnCl_2$ is also known, forming aryl-aryl bonds.[57]

Additionally, homo-coupling is possible with $MnCl_2$ as catalyst. An oxidant like dichloroethane must also be stoichiometrically added, resulting in good yields when using arenes bearing one substituent.[58] This reaction is shown Figure 28.

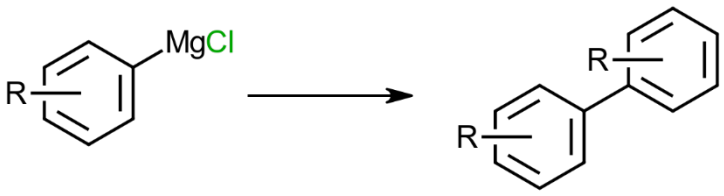


Figure 28 - Homo-coupling

1.2.5 C-H activation

A field that has seen a lot of research in the last decade is the activation of C-H bonds. They circumvent the need for pre-functionalisation and thus produce less waste. Unfortunately, some challenges do occur: especially selectivity is hard to achieve as there is most often more than one C-H bond that can potentially be activated. After activation, the bond can then either be oxidised or halogenated.[33]

There are a few examples of manganese-catalysed C-H activation that mostly utilise a porphyrin ring as ligand, as seen in Figure 29.[59]

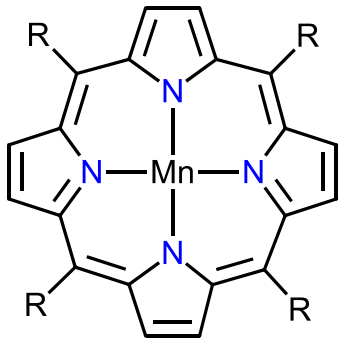


Figure 29 - Porphyrin-based catalysts for C-H activation

The porphyrin ring can also be modified with a number of different substituents, which can even be bridged.[60,61] In addition, a manganese(V) catalyst featuring cyanide ligands has been shown to activate and then oxidise C-H bonds with numerous different oxidising agents, the reaction with cyclohexane is shown in Figure 30.[62]

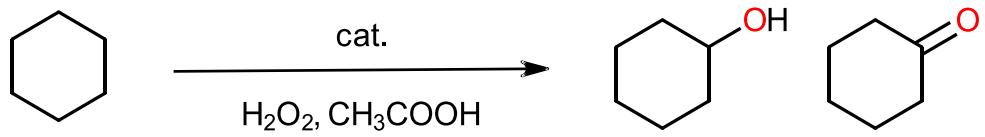


Figure 30 - C-H Activation and oxidation

2 Aim of the thesis

Hydrofunctionalisations are versatile and useful tools in synthetic chemistry to introduce certain functional groups into a molecule. Thus, a series of trials were conducted with a catalyst (Figure 31) that was previously known to be able to catalyse hydrogenation reactions on unactivated alkenes. Hydroboration, hydrothiolation and hydrophosphorylation on alkenes were among the reactions that were investigated.

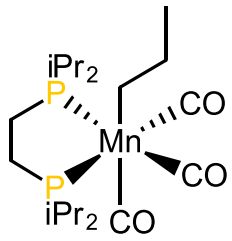


Figure 31 – Well-defined Mn(I)-catalyst used in this thesis

The first trails in hydroboration with pinacolborane showed the most promise. Hydroboration is especially useful in that regard as boranes can easily be converted in several other functional groups in a following step. That is why further studies were conducted to not only determine the optimal conditions like for example temperature, solvent, catalyst loading and such, but also the scope and limitations of this catalytic system. A reaction scheme is shown in Figure 32.

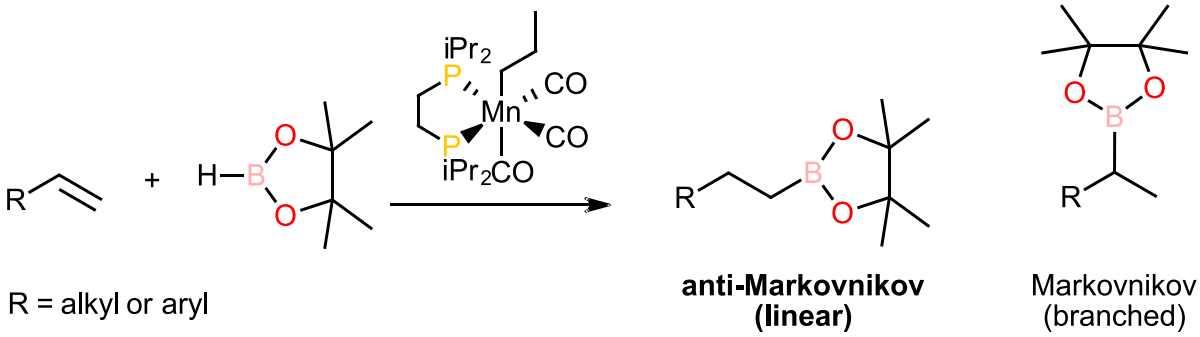


Figure 32 - Catalysed hydroboration reaction

3 Results and Discussion

3.1 Catalyst Synthesis

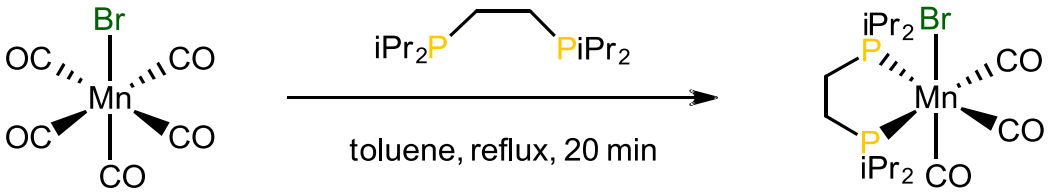


Figure 33 - Reaction of precursor with bidentate ligand

First step of the catalyst synthesis, as seen in Figure 33, was to react $Mn(CO)_5Br$ with the bidentate phosphine ligand 1,2-bis(di-isopropylphosphino)ethane (dippe). Hereby gas evolution could be observed as two CO-ligands got removed.

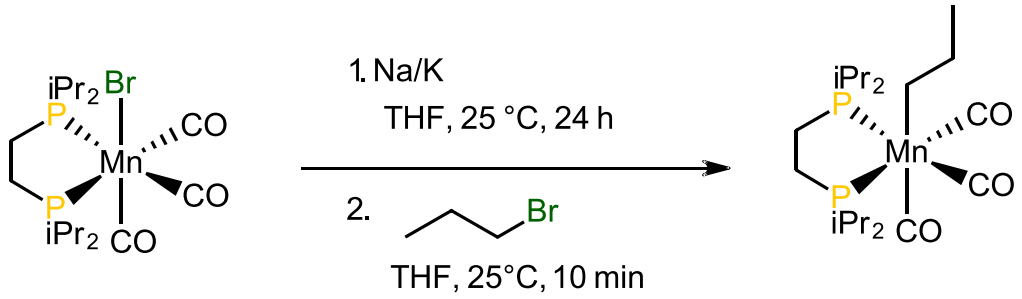


Figure 34 - Deprotonation and alkylation of complex

In the following step, as seen in Figure 34, sodium-potassium alloy was used for dehalogenation, after which it was reacted with 1-bromopropane. This resulted in the substitution of the bromide ligand with a propyl group, yielding the catalyst that was used for all further catalytic reactions.

3.2 Optimisation of reaction conditions

In order to determine the scope and limitations of the catalyst **17** for hydroboration, the reaction was to be optimised. For this purpose, the reaction of 4-chlorostyrene in combination with pinacolborane were chosen as model system (Figure 35).

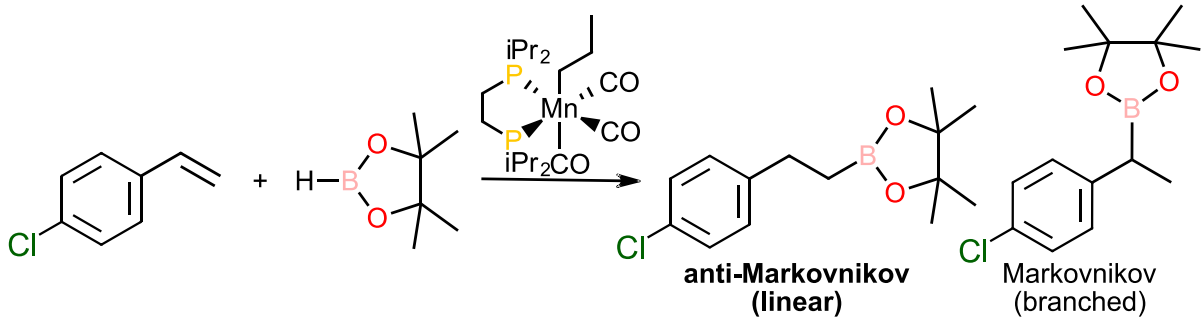


Figure 35 - General scheme for optimisation of reaction conditions

3.2.1 Impact of solvents

The first step in the optimisation procedure was to find a suitable solvent as it often impacts reactivity to a high degree. For that purpose, test reactions were conducted with the same reactants but with different solvents. Toluene as an apolar, THF as an aprotic polar and methanol as a protic polar solvent were used.

GC-MS was used for the determination of the conversion and linear to branched ratio. This was done by comparing the area of the mass peaks and subsequent analysis of the mass spectrum of all peaks.

Figure 36 depicts a GC spectrum of one of the optimisation reactions. The starting material, as it has a lower molecular mass than the hydroborated product, is the first that can be detected.

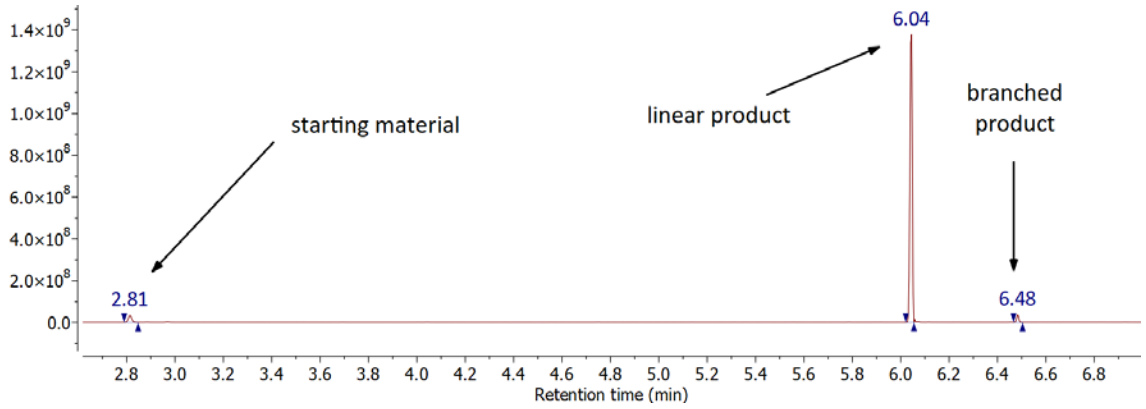


Figure 36 - GC of optimisation reaction with 4-chlorostyrene

The linear and branched isomers are also separated by gas chromatography, showing the ratio of the isomers. The mass spectrum of the hydroborated, linear product can be seen in Figure 37.

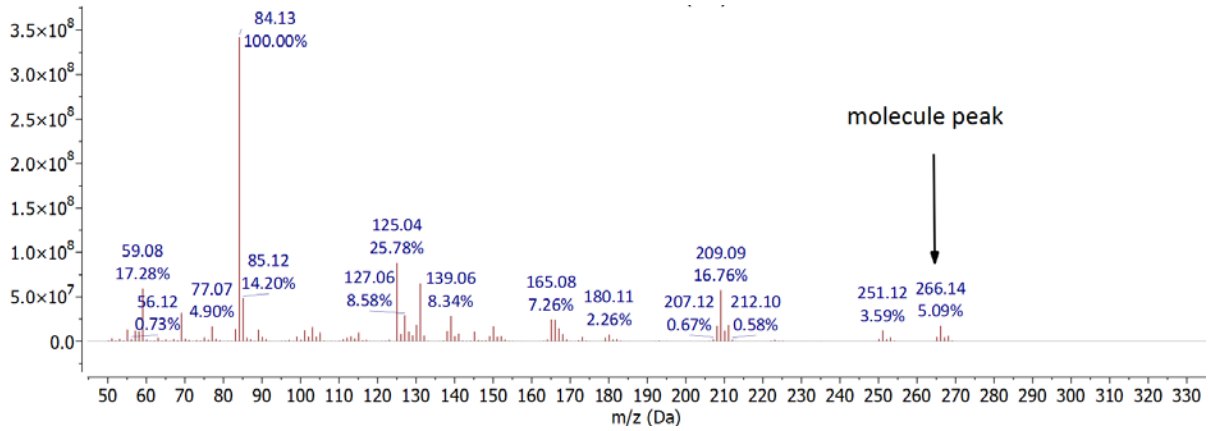


Figure 37 - Mass spectrum of the hydroborated product

During the optimisation reactions, two parameters were taken into consideration: First the conversion which had to be close to completion, and the linear-branched ratio. A ratio heavily on the side of one isomer was to be favoured. The reaction temperature was set to 70°C and the reaction time was 18 hours.

As can be seen in Table 1, apart from methanol, all other solvents including the neat reaction showed full conversion. Methanol reacted violently with pinacolborane; thus, it can be concluded that it forms an unreactive species. Out of the other three test reactions, THF had the best linear to branched ratio.

Table 1 - Solvent optimisation

Solvent	Conversion	Linear-branched ratio

neat	>99 %	96 - 4
toluene	>99 %	96 - 4
methanol	-	-
THF	>99 %	97 - 3

Reaction conditions: 1.12 mmol 4-Chlorostyrene, 1.15 mmol pinacolborane, 1 mol% catalyst, solvent (0.5 mL), 70°C, 18 h.

Another series of optimisation reactions were then conducted at lower catalyst loadings to determine the effect of the solvent on the conversion, as seen in Table 2. The best conversions could be achieved when using no solvent or THF. As the linear to branched ratio was again better when using THF, it was chosen as the solvent for all further catalysis.

Table 2 - Optimisation of solvents at lower catalyst loading

Solvent	Conversion	Linear-branched ratio
neat	88 %	97 - 3
toluene	82 %	98 - 2
THF	88 %	98-2

Reaction conditions: 1.12 mmol 4-Chlorostyrene, 1.15 mmol pinacolborane, 0.5 mol% catalyst, solvent (0.5 mL), 70°C, 18 h.

3.2.2 Further Optimisation

After determination of the optimal solvent, the reaction was to be optimised by changing parameters as the amount of catalyst and pinacolborane, the reaction time and the temperature. In Table 3, the first part of the optimisations is shown.

Table 3 - Optimisation part 1

Reaction time	Catalyst loading	Pinacolborane [eq.]	Conversion	Linear-branched ratio
18 h	1.0 mol%	1.02	>99 %	97 - 3

18 h	0.50 mol%	1.02	88 %	98 - 2
24 h	0.50 mol%	1.02	97 %	98 - 2
24 h	0.50 mol%	1.20	88 %	98 - 2
24 h	0.25 mol%	1.20	70 %	99 - 1
24 h	0.10 mol%	1.50	33 %	>99 - 1

Reaction conditions: 1.12 mmol 4-Chlorostyrene, 1.15 - 1.68 mmol pinacolborane, x mol% catalyst, THF (0.5 mL), 70°C, 18 - 24 h.

The first step was to decrease the catalyst loading to observe the effect on the conversion. As seen above, the conversion decreased to 88 % when halving the amount of catalyst. To compensate the lower catalyst loading, the reaction time was increased from 18 hours to 24 hours, resulting again in almost full conversion.

Then, trials were started to determine how much the catalyst loading could be lowered and what effect it would have on the conversion. To make up for the low amount of catalyst, the amount of pinacolborane was increased accordingly. However, the increased amount of pinacolborane had the opposite effect as desired: The conversion was comparatively lower, as too much borane seemingly inhibits the catalyst.

As it can be seen in Table 4, the following step was increasing the temperature, which resulted in full conversion, even with a slightly higher concentration of pinacolborane. The temperature was not increased any further as stability of all reactants had to be ensured. At 80°C, even at a catalyst loading of only 0.25 mol%, almost full conversion was achieved. These condition where thus chosen for the determination of the scope.

Table 4 - Optimisation part 2

Catalyst loading	Pinacolborane [eq.]	Conversion	Linear-branched ratio
0.50 mol%	1.20	>99 %	97 - 3
0.25 mol%	1.02	97 %	98 - 2
0.20 mol%	1.02	94 %	98 - 2
0.10 mol%	1.02	76 %	99 - 1

-	1.02	7 %	>99 - 1

Reaction conditions: 1.12 mmol 4-Chlorostyrene, 1.15 - 1.34 mmol pinacolborane, x mol% catalyst, THF (0.5 mL), 80°C, 24 h.

In addition, at 0.1 mol%, a conversion of 76 % could still be observed, which translates to a Turnover Number (TON) of around 760.

To further prove the activity of the catalyst, a blank reaction without catalyst was conducted at the respective conditions. A conversion of only 7 % could hereby be observed, which is significantly lower than the catalysed reaction.

3.3 Work-up

As the reaction conditions have been determined, a convenient work-up was ought to be found. The general scheme for the work-up is shown below in Figure 38.

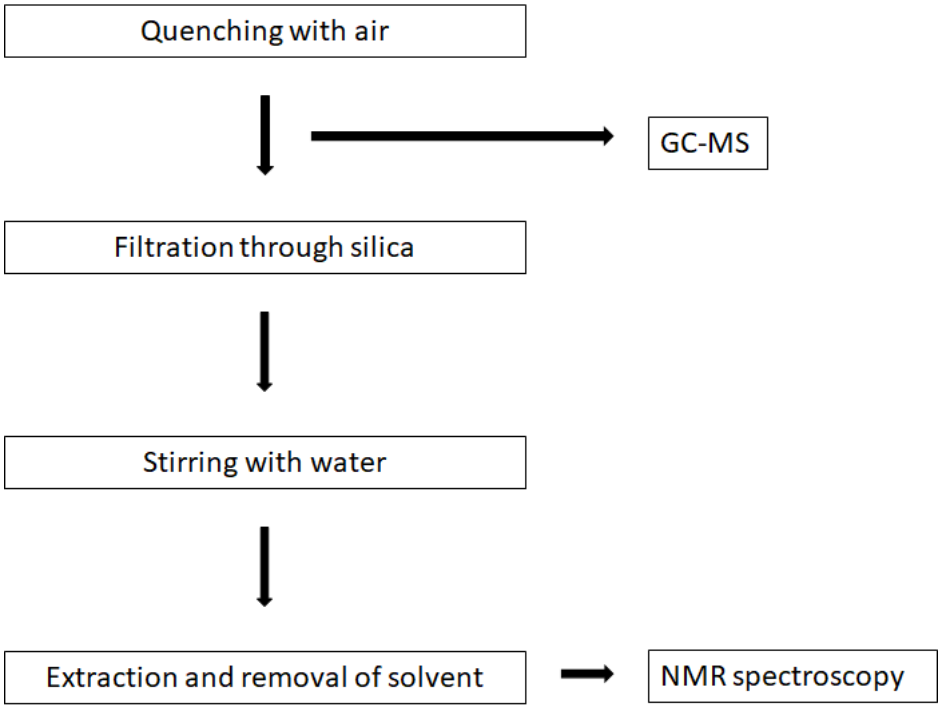


Figure 38 - Scheme for work-up of hydroboration reactions

The first step was simply to quench the reaction with oxygen as the catalytically active species is air sensitive. A small amount was taken right after for the measurement of a GC-MS to determine the conversion and linear-branched ratio.

After evaporation of THF, the sample was diluted with a solvent, and filtered through a pad of silica. This was done to remove the complex and remove other impurities that could have formed during the reaction. It was then stirred in water mainly to remove the hydrolysed species of pinacolborane (Figure 39).

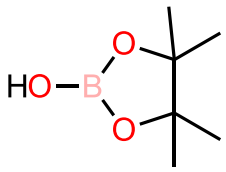


Figure 39 - Hydrolysed pinacolborane

This species could be detected by recording ^{11}B-NMR. One such spectrum is depicted in Figure 40.

This species mainly formed when not all pinacolborane was consumed in a reaction. It hydrolyses seemingly instantaneously when coming in contact with oxygen or water, which was inadvertent during work-up.

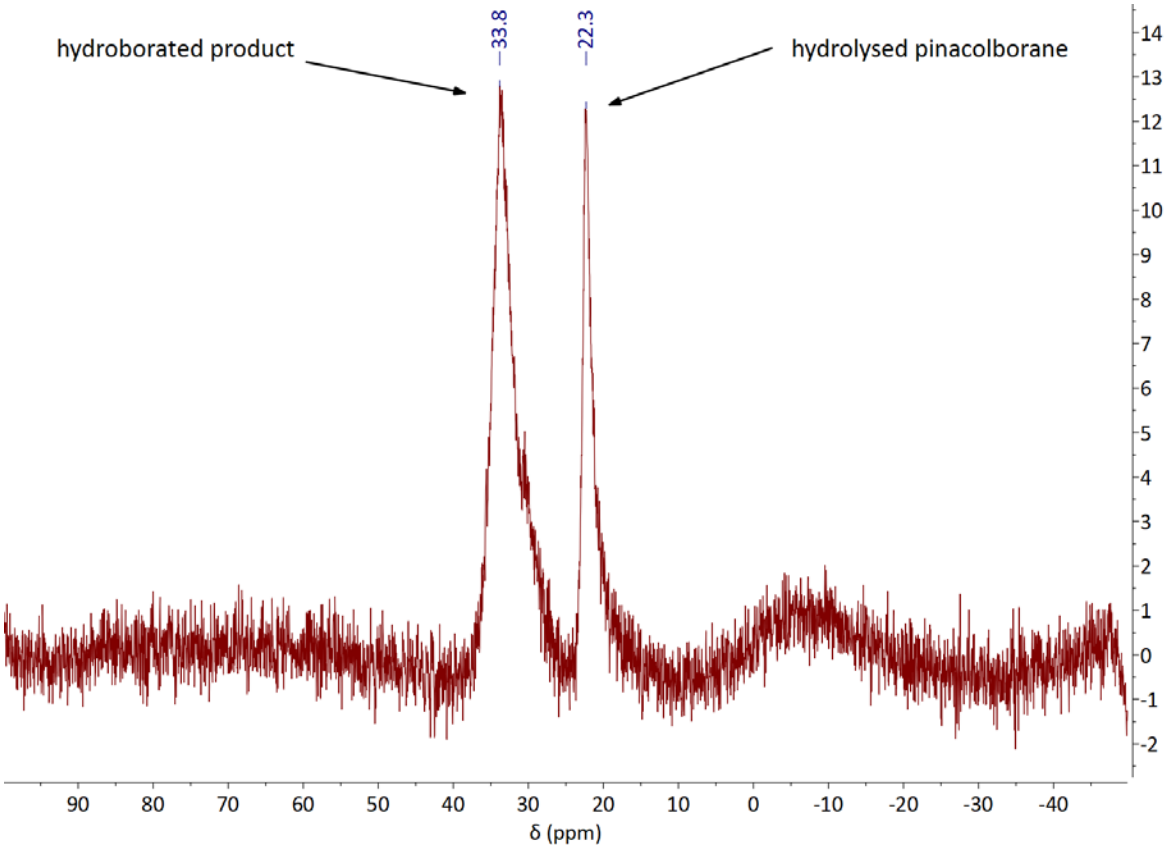


Figure 40 - ^{11}B-NMR spectrum of hydroborated styrene

Last step was to extract the product from the water and remove all solvents, yielding the pure product which was then analysed *via* NMR spectroscopy. Therefore, ^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded. It should be noted that no column chromatography at any time was needed to achieve pure products.

3.4 Scope and Limitation

To determine the substrate scope of the catalyst for hydroboration, a variety of alkenes were investigated. Styrene derivatives were among the first as they were already known to be reactive, as seen in the optimisation reactions. In the following step, other aromatic and aliphatic systems were tested. The reaction scheme is shown in Figure 41.

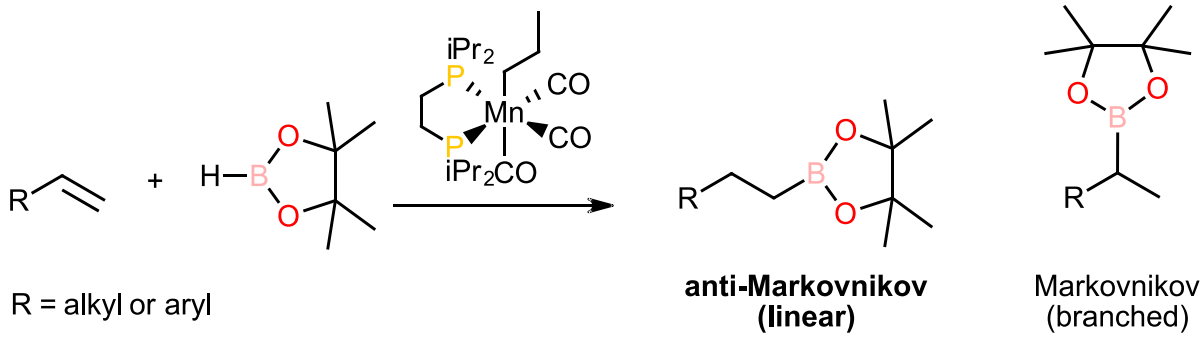
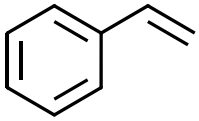
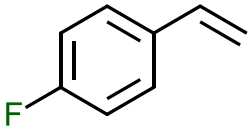
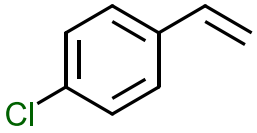


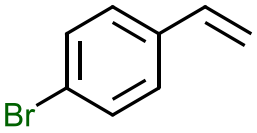
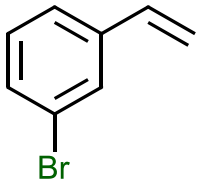
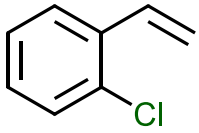
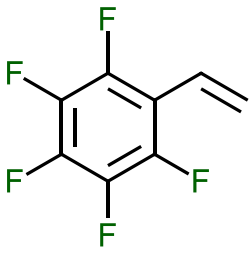
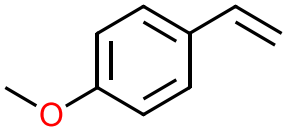
Figure 41 - Reaction scheme for determination of scope

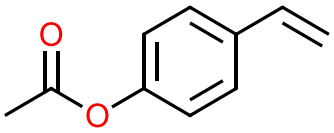
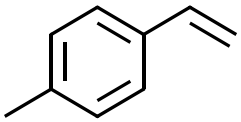
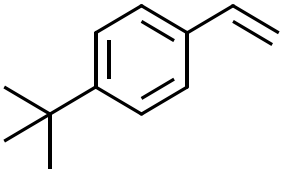
As depicted in Table 5, the best conversion can be achieved if no substituents are on the phenyl ring or if electron-withdrawing moieties like halogens are in the *para*-position to the vinyl group (entries **1-4**). If the halogen is in the *meta*-position, the conversion drops slightly comparatively (entry **5**), and drops again when in *ortho*-position (entry **6**), most likely due to the steric hinderance. If all positions besides the vinyl moiety in the phenyl ring are halogenated, the double bond is again strongly activated, leading to a full conversion (entry **7**).

Table 5 – Results of hydroboration of styrene derivatives

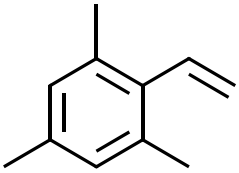
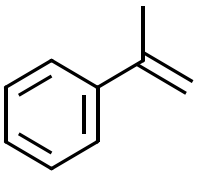
Entry	Substrate	Conversion calculated *via* GC-MS [%]	Isolated yield [%]	Linear to branched ratio
1		96	73	>99 - 1
2		>99	87	>99 - 1
3		97	90	>99 - 1

Continuation of Table 5

4		>99	82	>99 - 1
5		94	89	>99 - 1
6		91	83	99-1
7		>99	80	>99 - 1
8		85	69	>99 - 1

9		89	65	97-3
10		86	71	99-1
11		80	58	>99 - 1

Continuation of Table 5

12		95*	77	>99 - 1
13		14	-	>99 - 1

Reaction conditions: 1.12 mmol 4-chlorostyrene, 1.15 mmol pinacolborane, 0.25 mol% catalyst, THF (0.5 mL), 80°C, 24 h. *1 mol% catalyst

In case of electron-donating groups in *para*-position, the conversion decreases compared to electron-withdrawing groups, depending on the strength of the effect. Substituents like methoxy and acetyloxy, which donate electrons *via* resonance, still lead to good conversions (entries **8** and **9**), which are nonetheless lower than that of the halogens.

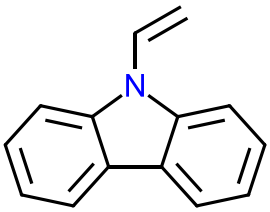
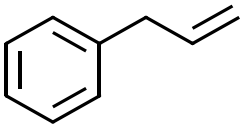
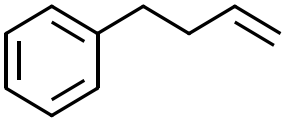
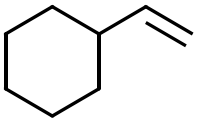
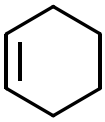
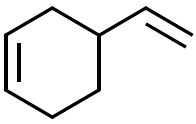
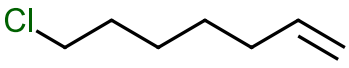
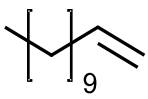
When comparing alkyl groups, a methyl group has a weaker donating effect than a tert-butyl group, resulting in a better conversion and vice versa (entries **10** and **11**). This trend continues as three methyl groups, one in *para* and two in *ortho* position, lead to significantly lower conversions and the need for a higher catalyst loading of 1 mol% (entry **12**). In addition to the electronic effect in this case, the double bond is also sterically more hindered. This effect is especially obvious with α-methylstyrene, which only showed very low conversion (entry **13**).

As seen in Table 4, excellent conversions could be achieved when using *N*-vinylcarbazole (entry **14**). This is contrary to the results before, as carbazole is quite an electron-rich aromatic system, which should lower the conversion. Good to excellent conversions can be achieved as well if the double bond is not conjugated to an aromatic system (entry **15** and **16**). The conversion even increases the further the double bond is away from the phenyl ring, most likely due to less steric hinderance.

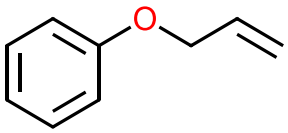
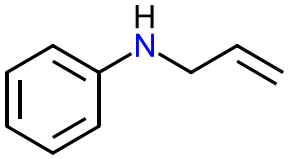
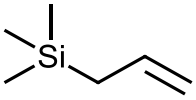
The hydroboration reaction also works with vinylcyclohexane, which showed a good conversion, proving that aliphatic systems can also be used (entry **17**). However, if the double bond is present within the ring, it is too sterically hindered which results in almost no conversion (entry **18**). This effect was exploited by using 4-vinylcyclohexene, where the

double bond within the ring is left untouched whereas the vinyl group is hydroborated (entry **19**). This proved the selectivity of the catalyst towards terminal alkenes and should be highlighted in this context.

Table 6 – Results of hydroboration of different aryl and alkyl substrates

Entry	Substrate	Conversion calculated *via* GC-MS [%]	Isolated yield [%]	Linear to branched ratio
14		98	75	>99 - 1
15		85	56	>99 - 1
16		92	75	>99 - 1
17		86	58	>99 - 1
18		<1	-	>99 - 1
19		88	69	98 - 2
20		86	79	>99 - 1
21		85	82	>99 - 1

Continuation of Table 7

22		50*	46	>99 - 1
23		81*	75	>99 - 1
24		Not possible*	48	Not possible

Reaction conditions: 1.12 mmol 4-chlorostyrene, 1.15 mmol pinacolborane, 0.25 mol% catalyst, THF (0.5 mL), 80°C, 24 h. *1 mol% catalyst

Linear alkenes were also efficiently hydroborated. 6-Chlorohexene showed good conversion, as well as 1-dodecene (entry **20** and **21**). In the case of 1-dodecene, in addition to the hydroborated product, multiple isomers could be detected where the double bond migrated, as seen in Figure 42. The amount of isomerised product was quite low, which indicates only a slight tendency for this kind of reaction.

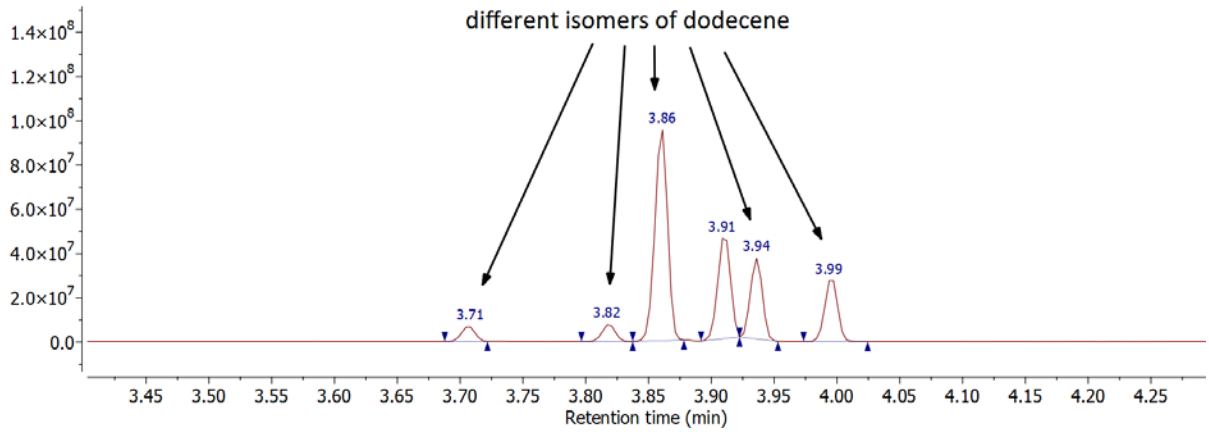


Figure 42 - GC of dodecene after hydroboration reaction

In the last step, substrates with functional groups in close proximity to the C-C double were investigated. In these cases, a catalyst loading of 1 mol% had to be employed. The ether containing substrate (entry **22**) gave moderate results, whereas the aniline-based substrate gave good yields (entry **23**). The conversion of the silane-containing substrate could not be

analysed as the GC-MS did not show any peak for the starting material, even after several tries. Thus, only isolated yield was able to be determined which was moderate (entry **24**).

Compared to existing manganese-based catalysts for the hydroboration of alkenes, there is only one catalyst who affords the linear product as of writing this thesis. It operates at catalyst loadings of 2 mol% and requires 6 mol% sodium *tert*-butoxide to form the catalytically active species.[50] In this work, a much lower catalyst loading of 0.25 mol% is needed and no additional bases have to be added, which is of advantage especially for sensitive substrates .

Additionally, the catalysis in this work affords better conversions when the substrate bears electron withdrawing groups. This is in contrast with the mentioned catalyst by Thomas et al. which had better conversions with electron donating groups.[50]

3.6 Outlook

After determination of the scope, mechanistic studies for this reaction would be of interest. Especially the detection of intermediates and theoretical calculations would give great insight into limiting factors during the catalysis.

Apart from alkenes, other functional groups could also be hydroborated, some examples being kentones, carboxylic acids, nitriles and alkynes. The hydroboration of ketones is promising since the catalyst is catalytically active for this hydrofunctionalisation reaction. First preliminary studies exhibited good conversions at temperatures of 50°C.

Furthermore, the utilisation of a different manganese-based complex featuring a PN or NN bidentate ligand could be of interest for further catalytic studies. Since PP bidentate ligand systems have been proven to be catalytically active towards a multitude of different reactions and substrates, chemically similar complexes could exhibit similar or even enhanced properties.

4 Conclusion

In this work, a well-defined manganese(I) catalyst was utilised for the hydroboration of a wide variety of different terminal alkenes.

At first, reaction conditions were optimised to achieve excellent conversion of 4-chlorostyrene as test substrate while keeping the amount of catalyst as low as possible. Special emphasis was put on not reaching a temperature where most substrates would decompose, which was successful.

Additionally, work-up was optimised to be easy, quick and applicable to all substrates. The use of column-chromatography was successfully omitted for all substrates as NMR spectroscopy showed no impurities.

Finally, scope of the catalyst was determined. Therefore, different aryl and alkyl substrates featuring different moieties were hydroborated, determining conversion and yield of each respective substrate. The catalyst showed high tolerance towards a variety of different functional groups, for examples halides, ethers and amines. Especially aryl compounds bearing an electron-withdrawing group in *para*-position had excellent conversions. Additionally, a large number of alkyl substrates could be successfully hydroborated, highlighting the broad substrate scope of the catalyst.

5 Experimental Part

5.1 Materials and methods

All used reagents and solvents were purchased from commercial suppliers and directly used without further purification, if not stated otherwise. Anhydrous MeOH, THF and toluene were dried over molecular sieve.

^{1}H-, ^{11}B- and ^{13}C{^{1}H}-NMR were recorded in chloroform-*d* or methylene chloride-d_2 solution on a Bruker Avance 250 (250 MHz) or Bruker Avance 400 (400 MHz). All chemical shifts (δ) are reported in ppm, using tetramethylsilane for ^{1}H-, boron trifluoride diethyl etherate for ^{11}B- and tetramethylsilane for ^{13}C{^{1}H}-NMR spectra. All coupling constants (J) are reported in Hertz (Hz). The following abbreviations are used to describe multiplets: s = singlet, d = duplet, t = triplet, m = multiplet.

GC–MS analysis was conducted on a ISQ LT Single quadrupole MS (Thermo Fisher) directly interfaced to a TRACE 1300 Gas Chromatographic systems (Thermo Fisher), using a Rxi-5Sil MS (30 m, 0.25mm ID) cross-bonded dimethyl polysiloxane capillary column at a carrier flow of He 1.5 mL/min. The oven program temperature was:

Method **A**: 100°C (2 min)//35 °C/min//300 °C (4 min)

Method **B**: 40°C (2.5 min)//12°C/min//220 (2.5 min)

If not stated otherwise, Method **A** was used as default.

5.2 Synthesis of complex

Catalyst **17** was synthesised by a modified procedure from literature.[42] $MnBr(CO)_5$ (172 mg, 0.62 mmol, 1 eq.) was suspended in toluene (10 mL). To this mixture, a solution of dippe (164 mg, 0.62 mmol, 1 eq.) in toluene (10 mL) was added, allowing the evolved CO to vent. It was then refluxed for 5 minutes. After that, the yellow solution was evaporated. The crude complex was used without further purification.

To a solution of fac-[$Mn(dippe)(CO)_3(Br)$] (300 mg, 0.62 mmol, 1 eq.) in anhydrous THF (30 mL) Na/K alloy (2:3, 110 mg, 3.33 mmol) was added and the mixture was stirred for three days. Then 1-bromopropane (5 mL) was added and stirred for 2 h. Upon removal of the solvent

under vacuum, a yellow oil was obtained which was extracted with *n*-pentane. The solvent was removed and the residue washed with small amounts of *n*-pentane yielding 185 mg (67 %) of *fac*-[Mn(dippe)$(CO)_3(CH_2CH_2CH_3)$] as colourless solid (Catalyst **17**).

5.3 Hydroboration reactions

5.3.1 General procedure for optimisation reactions

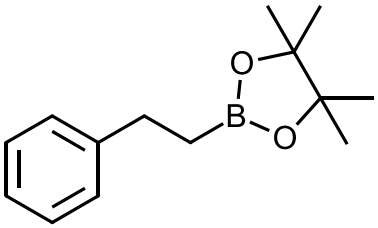
Inside an argon flushed glovebox, a screw cap vial (8 mL) was charged with 4-chlorostyrene (143 µL, 1.12 mmol, 1 eq.), pinacolborane, catalyst, solvent (0.5 mL) and closed under argon atmosphere. The vial was transferred out of the glovebox and stirred 18 to 24 hours at the indicated temperature. The sample was allowed to reach room temperature and exposed to air to quench the catalyst. 2 µL of the reaction mixture were dissolved in approximately 1.5 mL diethyl ether, filtered through a syringe filter, and analysed with GC-MS.

5.3.2 General procedure for determination of substrate scope

Inside an argon flushed glovebox, a screw cap vial (8 mL) was charged with substrate (1.12 mmol, 1 eq.), pinacolborane (166 µL, 1.15 mmol, 1.02 eq.), catalyst, THF (0.5 mL) and closed under argon atmosphere. The vial was transferred out of the glovebox and stirred 24 hours at 80°C. The sample was allowed to reach room temperature and exposed to air to quench the catalyst. 2 µL of the reaction mixture were dissolved in approximately 1.5 mL diethyl ether, filtered through a syringe filter, and analysed with GC-MS. The remaining mixture was subsequently filtered through a thin pad of *silica* with a solvent. It was then stirred for around 2 minutes with water (0.5 mL), extracted with approximately 5 mL solvent and dried in *vacuo* to yield the pure product.

5.3.3 Scope and Limitations

4,4,5,5-Tetramethyl-2-(2-phenylethyl)-1,3,2-dioxaborolane (Product **1**)



Styrene (129 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 0.25 mol%); eluent: mixture of *n*-pentane and diethylether (10:1); extracted with *n*-pentane; 190 mg (73 %) of a colourless oil.

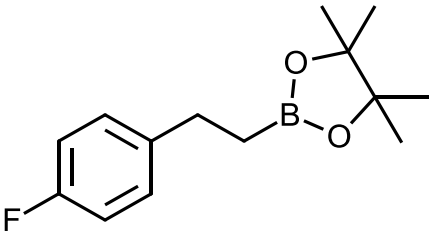
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40 – 7.20 (m, 5H), 2.73 (t, *J* = 8.1 Hz, 2H), 1.20 (s, 12H), 1.12 (t, *J* = 7.7 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 144.4, 128.2, 128.1, 125.6, 83.1, 30.0, 24.9, 13.0 ppm.

RT (GC): 5.35 min MS: 232.22 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

2-[2-(4-Fluorophenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **2**)



4-Fluorostyrene (134 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 246 mg (87 %) of a colourless oil.

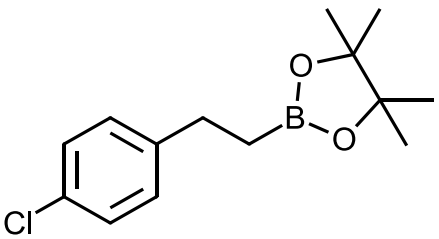
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 6.7 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.11 (t, *J* = 7.6 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 161.2 (d, *J* = 242.8 Hz), 140.0 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 7.7 Hz), 114.9 (d, *J* = 21.0 Hz), 83.2, 29.2, 24.8, 13.4 ppm.

RT (GC): 5.54 min MS: 250.20 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

4,4,5,5-Tetramethyl-2-[2-(4-Chlorophenyl)ethyl] -1,3,2-dioxaborolane (Product **3**)



4-Chlorostyrene (143 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 271 mg (90 %) of a colourless oil.

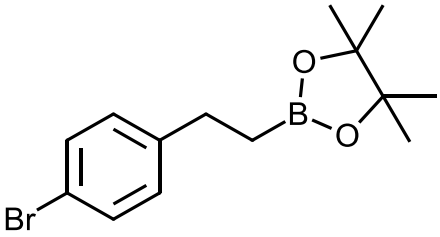
^{1}H NMR (250 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 7.17 – 7.10 (m, 2H), 2.71 (t, *J* = 7.9 Hz, 2H), 1.21 (s, 12H), 1.15 – 1.07 (m, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 143.0, 131.3, 129.5, 128.4, 83.3, 29.5, 24.9, 13.0 ppm.

RT (GC): 6.22 min MS: 266.06 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

2-[2-(4-Bromphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **4**)



4-Bromostyrene (147 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 288 mg (82 %) of a colourless oil.

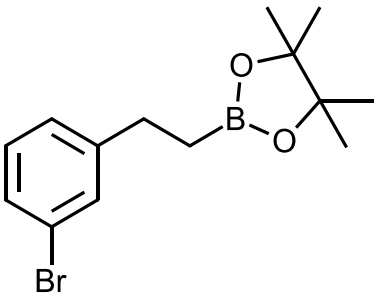
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.69 (t, *J* = 8.1 Hz, 2H), 1.21 (s, 12H), 1.10 (t, *J* = 8.2 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 143.3, 131.2, 129.8, 119.2, 83.1, 29.4, 24.8, 12.9 ppm.

RT (GC): 6.56 min MS: 310.14, 312.14 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

2-[2-(3-Bromophenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **5**)



3-Bromostyrene (147 µL, 1.13 mmol, 1 eq); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 310 mg (89 %) of a colourless oil.

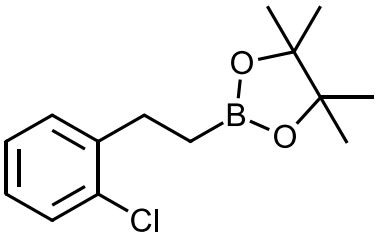
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.37 (s, 1H), 7.30 – 7.26 (m, 1H), 7.16 – 7.11 (m, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.19 (s, 12H), 1.06 (t, *J* = 8.0 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 147.5, 131.5, 130.2, 128.9, 127.2, 122.5, 83.5, 30.1, 25.0, 13.8 ppm.

RT (GC): 6.48 min MS: 309.99, 311.99 m/z $[M]^+$

These spectroscopic data correspond to reported data.[64]

2-[2-(2-Chlorophenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **6**)



2-Chlorostyrene (144 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 248 mg (83 %) of a colourless oil.

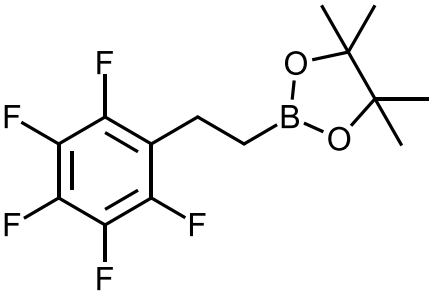
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.34 – 7.26 (m, 2H), 7.21 – 7.07 (m, 2H), 2.85 (t, *J* = 8.3 Hz, 2H), 1.25 (s, 12H), 1.16 (t, *J* = 8.0 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 145.1, 133.9, 129.9, 129.4, 127.1, 126.7, 83.3, 27.9, 24.9, 11.8 ppm.

RT (GC): 6.18 min MS: 266.05 m/z $[M]^+$

These spectroscopic data correspond to reported data.[65]

2-[2-(2,3,4,5,6-Pentafluorophenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **7**)



2,3,4,5,6-Pentafluorostyrene (155 µL, 1.13 mmol, 1 eq); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 291 mg (80 %) of a colourless oil.

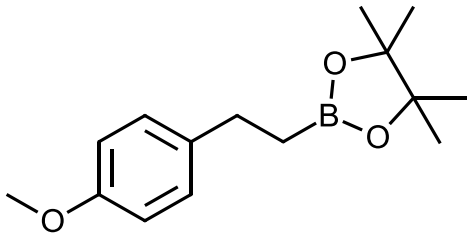
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.78 (t, *J* = 8.2 Hz, 2H), 1.23 (s, 12H), 1.10 (t, *J* = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 83.5, 24.8, 17.0, 11.3 ppm, C-F was not detected

RT (GC): 5.11 min MS: 322.19 m/z $[M]^+$

These spectroscopic data correspond to reported data.[64]

2-[2-(4-Methoxyphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **8**)



4-Methoxystyrene (150 µL, 1.13 mmol, 1 eq); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: mixture of *n*-pentane and diethylether (40:1); extracted with *n*-pentane; 204 mg (69 %) of a slightly yellow oil.

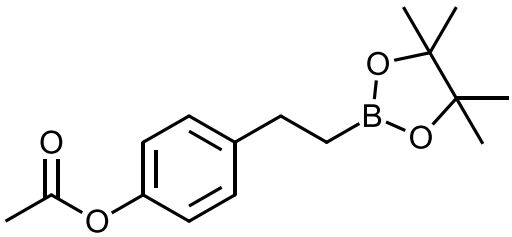
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.75 (s, 3H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.19 (s, 12H), 1.08 (t, *J* = 8.2 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 157.6, 136.6, 128.9, 113.6, 83.1, 55.2, 29.1, 24.8, 13.2 ppm.

RT (GC): 6.22 min MS: 262.21 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

4-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl acetate (Product **9**)



4-Vinylphenyl acetate (172 µL, 1.13 mmol, 1 eq); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 213 mg (65 %) of a colourless oil.

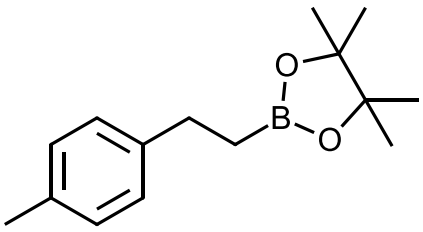
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.22 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 2.72 (t, *J* = 8.1 Hz, 2H), 2.25 (s, 3H), 1.21 (s, 12H), 1.09 (t, *J* = 8.2 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 170.4, 149.5, 143.0, 129.7, 122.1, 83.9, 30.2, 25.4, 21.7, 13.9 ppm.

RT (GC): 17.64 min MS: 290.25 m/z $[M]^+$ (Method **B**)

These spectroscopic data correspond to reported data.[63]

4,4,5,5-Tetramethyl-2-[2-(p-tolyl)ethyl]-1,3,2-dioxaborolane (Product **10**)



4-Methylstyrene (148 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 197 mg (71 %) of a colourless oil.

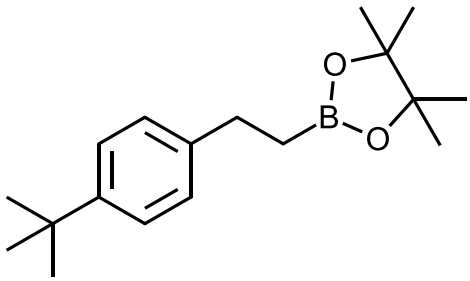
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22 – 7.06 (m, 4H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.21 (s, 12H), 1.10 (t, *J* = 8.7 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 141.4, 134.9, 128.9, 127.9, 83.1, 29.5, 24.8, 21.0, 13.0 ppm.

RT (GC): 5.70 min MS: 246.21 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

2-[2-(4-tert-Butylphenyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **11**)



4-tert-Butylstyrene (206 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 188 mg (59 %) of a colourless oil.

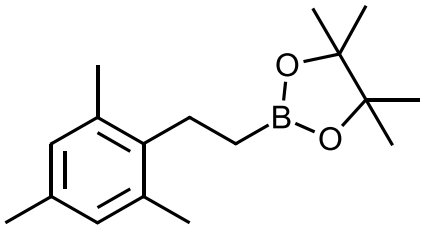
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.33 - 7.23 (m, 2H), 7.21 – 7.01 (m, 2H), 2.69 (t, J = 8.3 Hz, 2H), 1.28 (s, 9H), 1.20 (s, 12H), 1.11 (t, J = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 148.3, 141.4, 127.8, 125.1, 83.1, 31.6, 31.4, 29.5, 24.9, 13.2 ppm.

RT (GC): 17.00 min; MS: 288.26 m/z $[M]^+$ (Method **B**)

These spectroscopic data correspond to reported data.[64]

4,4,5,5-Tetramethyl-2-[2-(2,4,6-Trimethylphenyl)ethyl]- 1,3,2-dioxaborolane (Product **12**)



2,4,6-Trimethylstyrol (180 µL, 1.13 mmol, 1 eq.); catalyst (5 mg, 11.3 µmol 1 mol%), eluent: *n*-pentane, extracted with *n*-pentane; 236 mg (77 %) of a colourless oil.

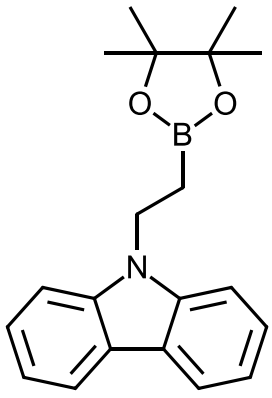
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83 (s, 2H), 2.69 (t, *J* = 8.7 Hz, 2H), 2.32 (s, 6H), 2.26 (s, 3H), 1.29 (s, 12H), 0.98 (t, *J* = 8.8 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 138.6, 135.7, 134.7, 128.9, 83.2, 25.0, 23.4, 20.9, 19.8, 11.4 ppm.

RT (GC): 6.52 min MS: 274.13 m/z $[M]^+$

These spectroscopic data correspond to reported data.[66]

9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)9H-carbazole (Product **13**)



N-Vinylcarbazole (218 mg, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: dichloromethane; extracted with dichloromethane; 272 mg (75 %) of a slightly yellow solid.

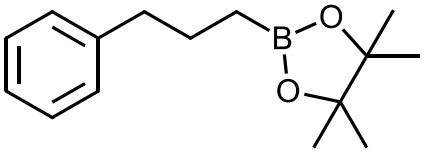
^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.38 (m, 4H), 7.29 – 7.16 (m, 2H), 4.47 (t, *J* = 8.0 Hz, 2H), 1.42 (t, *J* = 7.4 Hz, 2H), 1.21 (s, 12H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 140.0, 125.5, 123.0, 120.3, 118.7, 109.1, 83.6, 38.8, 24.9, 11.8 ppm.

RT (GC): 8.45 min MS: 321.26 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (Product **14**)



Allylbenzene (149 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: mixture of *n*-pentane and diethylether (10:1); extracted with *n*-pentane; 155 mg (56 %) of a colourless oil.

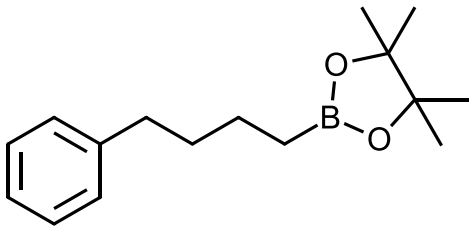
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.46 – 7.12 (m, 5H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.70 (t, J = 7.7 Hz, 2H), 1.21 (s, 12H), 0.79 (t, *J* = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 142.7, 128.6, 128.2, 125.6, 82.9, 38.6, 26.2, 24.9, 11.2 ppm.

RT (GC): 15.34 min MS: 246.25 m/z $[M]^+$ (Method **B**)

These spectroscopic data correspond to reported data.[63]

4,4,5,5-Tetramethyl-2-(4-Phenylbutyl) -1,3,2-dioxaborolane (Product **15**)



4-Phenylbutene (169 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 218 mg (75 %) of a colourless oil.

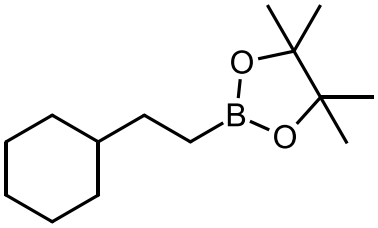
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.25 – 7.09 (m, 5H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.71 – 1.52 (m, 2H), 1.52 – 1.39 (m, 2H), 1.21 (s, 12H), 0.78 (t, *J* = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.1, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 23.9, 11.4 ppm.

RT (GC): 6.28 min MS: 260.13 m/z $[M]^+$

These spectroscopic data correspond to reported data.[65]

2-[2-(cyclohexyl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **16**)



Vinylcyclohexane (114 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 155 mg (58 %) of a colourless oil.

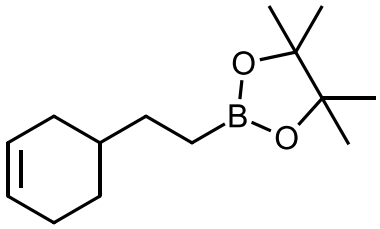
^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.79 – 1.55 (m, 4H), 1.35 – 1.04 (m, 19H), 0.87 (t, *J* = 6.1 Hz, 2H), 0.75 (t, *J* = 8.3 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (63 MHz, $CDCl_3$): δ = 82.9, 40.0, 33.1, 31.4, 26.8, 26.5, 24.9, 8.14 ppm.

RT (GC): 13.85 min MS: 238.23 m/z $[M]^+$ (Method **B**)

These spectroscopic data correspond to reported data.[63]

2-[2-(3-cyclohexen-1-yl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **17**)



4-Vinylcyclohexene (146 µL, 1.13 mmol, 1 eq; catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 184 mg (69 %) of a colourless oil.

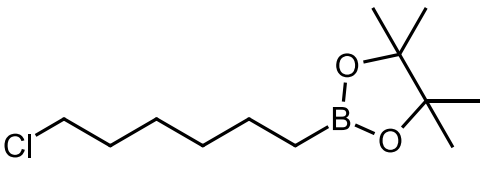
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.64 (d, *J* = 2.0 Hz, 2H), 2.14 – 1.98 (m, 3H), 1.79 – 1.70 (m, 1H), 1.66 – 1.56 (m, 1H), 1.50 – 1.39 (m, 1H), 1.38 – 1.30 (m, 2H), 1.21 (s, 12H), 1.19 – 1.11 (m, 1H), 0.75 (t, *J* = 8.2 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 127.3, 127.0, 83.2, 36.2, 32.1, 31.2, 29.0, 25.8, 25.1, 8.7 ppm.

RT (GC): 14.17 min MS: 236.15 m/z $[M]^+$ (Method **B**)

These spectroscopic data correspond to reported data.[63]

2-(6-Chlorohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **18**)



6-Chlorohexene (149 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 219 mg (79 %) of a colourless oil.

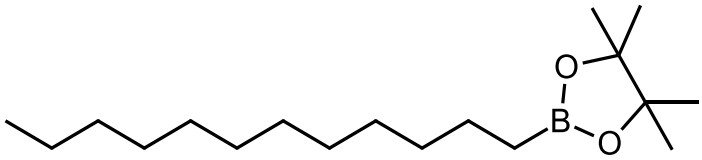
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.51 (t, *J* = 6.8 Hz, 2H), 1.82 – 1.69 (m, 2H), 1.47 – 1.36 (m, 4H), 1.36 – 1.27 (m, 2H), 1.23 (s, 12H), 0.76 (t, *J* = 7.6 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 83.0, 45.3, 32.7, 31.7, 26.8, 24.9, 23.9, 11.2 ppm.

RT (GC): 5.50 min MS: 246.06 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

2-Dodecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Product **19**)



1-Dodecene (250 µL, 1.13 mmol, 1 eq.); catalyst (1.25 mg, 2.8 µmol, 0.25 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 272 mg (82 %) of a colourless liquid.

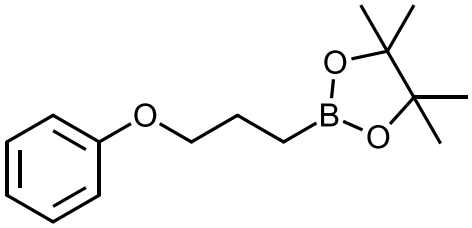
^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.36 – 1.23 (m, 21H), 1.21 (s, 12H), 0.88 (t, *J* = 6.4 Hz, 2H), 0.71 (t, *J* = 7.2 Hz, 2H).

^{13}C {^{1}H} NMR (63 MHz, CD_2Cl_2): δ = 83.1, 32.8, 32.4, 30.1, 30.1, 30.0, 29.9, 29.8, 25.0, 24.5, 23.1, 14.3, 11.1 ppm.

RT (GC): 6.63 min MS: 296.41 m/z $[M]^+$

These spectroscopic data correspond to reported data.[67]

4,4,5,5-Tetramethyl-2-(3-phenoxypropyl)-1,3,2-dioxaborolane (Product **20**)



Allyl phenyl ether (154 µL, 1.13 mmol, 1 eq); catalyst (5 mg, 11.3 µmol, 1 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 135 mg (46 %) of a colourless oil.

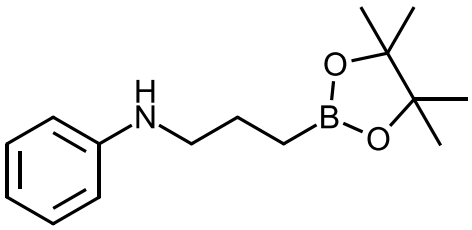
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.22 (m, 2H), 6.93 – 6.86 (m, 3H), 3.93 (t, *J* = 6.7 Hz, 2H), 1.91 – 1.80 (m, 2H), 1.23 (s, 12H), 0.88 (t, *J* = 7.9 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 159.22, 129.32, 120.29, 114.47, 83.00, 69.50, 24.63, 23.79, 7.20 ppm.

RT (GC): 4.41 min MS: 227.13 m/z $[M]^+$

These spectroscopic data correspond to reported data.[67]

[3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]aniline (Product **21**)



N-Allylaniline (153 µL, 1.13 mmol, 1 eq.); catalyst (5 mg, 11.3 µmol, 1 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 222 mg (75 %) of a yellow oil.

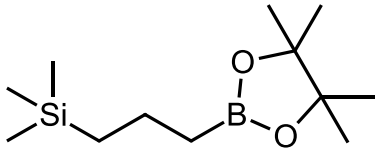
^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.13 (t, *J* = 7.6 Hz, 2H), 6.72 – 6.52 (m, 3H), 3.82 (s, 1H), 3.15 – 3.03 (m, 2H), 1.70 (t, *J* = 7.2 Hz, 2H), 1.24 (s, 12H), 0.84 (t, *J* = 7.5 Hz, 2H) ppm.

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 149.2, 129.5, 117.1, 112.9, 83.5, 46.4, 25.1, 24.8, 9.2 ppm.

RT (GC): 6.79 min MS: 261.11 m/z $[M]^+$

These spectroscopic data correspond to reported data.[68]

Trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]silane (Product **22**)



Allyltrimethylsilane (179 µL, 1.13 mmol, 1 eq); catalyst (1.25 mg, 11.3 µmol, 1 mol%); eluent: *n*-pentane; extracted with *n*-pentane; 130 mg (48 %) of a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 – 1.33 (m, 2H), 1.23 (s, 12H), 0.85 – 0.73 (m, 2H), 0.54 – 0.42 (m, 2H), -0.05 (s, 9H) ppm.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 83.0, 25.0, 20.2, 18.7, 15.6, -1.5 ppm.

RT (GC): 4.41 min MS: 227.13 m/z $[M]^+$

These spectroscopic data correspond to reported data.[63]

6 Appendix

6.1 List of abbreviations

BH_3 ..... monoborane
Bn ..... benzyl
CH_2Cl_2 ..... dichloromethane
CO_2 ..... carbon dioxide
Cp* ..... pentamethylcyclopentadiene
DBU ..... 1,8-diazabicyclo(5.4.0)undec-7-ene
dippe ..... 1,2-bis(di-isopropylphosphino)ethane
GC ..... gas chromatography
iPr ..... *iso*-propyl
KHMDS ..... potassium bis(trimethylsilyl)amide
$KMnO_4$ ..... potassium permanganate
$LiAlH_4$ ..... lithium aluminium hydride
LiOTf ..... lithium triflate
MeOH ..... methanol
Mes ..... mesityl
$MnCl_2$ ..... manganese(II) chloride
$Mn_2(CO)_{10}$ ..... dimanganese decacarbonyl
$Mn(CO)_5Br$ ..... bromopentacarbonylmanganese(I)
MS ..... mass spectroscopy
$NaBH_4$ ..... sodium borohydride
$NaBHEt_3$ ..... sodium triethylborohydride
NaOH ..... sodium hydroxide
nBu ..... butyl
NMR ..... nuclear magnetic resonance
OAc ..... acetyloxy
OTf ..... triflate
Ph ..... phenyl
tBu ..... *tert*-butyl
THF ..... tetrahydrofuran
TMS ..... trimethylsilyl

6.2 List of figures

6.3 List of tables

7 References

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