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Transborylation reaction of alkenyl boranes with diboron reagents and *gem*-diboryl alkanes

MASTER THESIS

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ABBREVIATIONS AND ACRONYMS

BBN	*9-Borabicyclo(3.3.1)nonane*
cat	*Catechol*
Cy	*Cyclohexyl*
dan	*naphthalene-1,8-diamine*
DCM	*Dichloromethane*
gem	*Geminal*
h	*Hours*
hex	*Hexylene glycolato*
HFIP	*1,1,1,3,3,3-hexafluoroisopropanol*
min	*Minutes*
neo	*Neopenthyl glycolato*
NMR	*Nuclear Magnetic Resonance*
pai	*(1S,2S,3R,5S)-(+)-Pinanediol*
Ph	*Phenyl*
pin	*Pinacol*
rt	*Room temperature*
THF	*Tetrahydrofuran*
TMP	*2,2,6,6-tetramethylpiperidine*

Acknowledgements

First of all, I want to thank Dra. Elena Fernández for giving me the chance to be part of her amazing research group. I am glad to have lived this experience here. Thank you for believing in me, for the motivation you always transmit and for sharing your experiences. Being part of your group has definitely prepared me for the future. I wish the best for you!

Next, I feel the need to be extremely grateful to all the current members of CatBorChem group. Thank you for always being super-nice and for all the time we spend together. You have taught me everything I know about columns with patience and kindness. I wish you the best in life!

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And last but not least, thanks to all the current members of the innCAT group. All of you have shown me that hard work can be rewarded. Thank you for your knowledge and your advices. I wish you the best of luck!

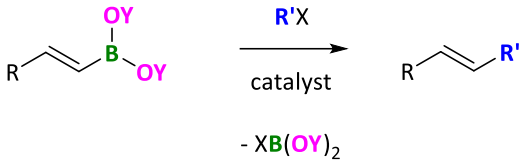
To my family and friends, thank you for your endless support and love. I know I can count on you, now and ever. To my boyfriend, who I met almost three years ago and, since then, we have helped and supported each other to achieve where we are. Thanks for everything!

1. Abstract

Exchange of boryl moieties between alkenyl boranes and diboron reagents has been postulated as a cross-metathesis pathway with concomitant formation of mixed diboron reagents. The stereocontrol of the sequence is guaranteed throughout the transborylation methodology. Herein, we describe the synthesis and characterization of different types of transborylated products. Finally, preliminary studies on the transborylation reaction between alkenyl boranes and *gem*-diboryl alkanes, with the subsequent formation of mixed unsymmetrical *gem*-diboryl alkanes, are disclosed.

2. Introduction

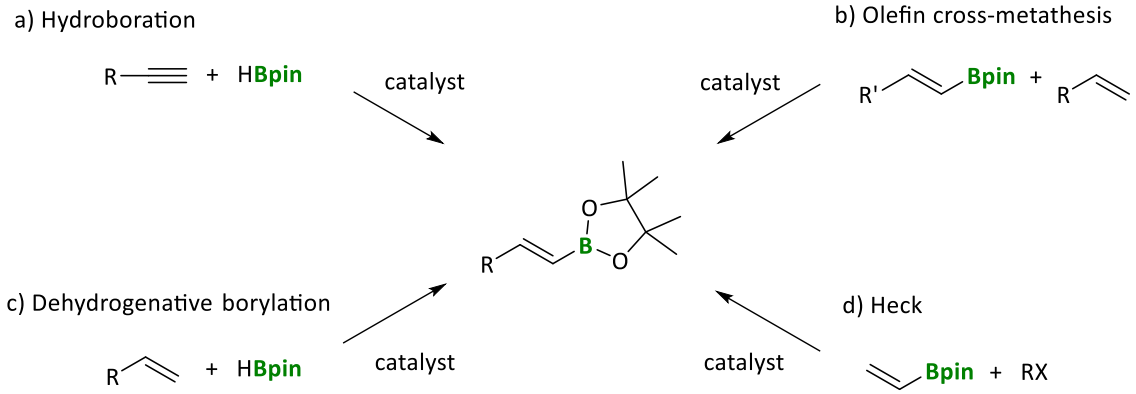
One of the most relevant goals for the organic synthetic community, is the accessibility to functionalized molecules. In that context, over the last decades, alkenyl boronates have been considered powerful intermediates for the functionalization of alkenes.[1,2] In particular, *E*-alkenyl boronates have become essential building blocks for the elaboration of functionalized alkenyl groups with retention of the stereoselectivity (Scheme 1).



Scheme 1. Model reaction for functionalization of *E*-alkenyl boronates.

The synthesis of *E*-alkenyl boronates can be performed through complementary strategies. The most extended methodology is the one based on hydroboration of alkynes, through *syn*-addition of B–H to C–C triple bond (Scheme 2a).[3,4,5] Alternatively, olefin cross-metathesis has been applied for the preparation of alkenyl boronates in the presence of Grubbs first generation catalysts (Scheme 2b).[6] Another strategy for the synthesis of *E*-alkenyl boronates can be conducted through dehydrogenative borylation of alkenes, catalyzed mainly by rhodium complexes,[7] although palladium,[8] iron,[9] cobalt[10] or copper,[11] can also be employed to catalyze this transformation (Scheme 2c).

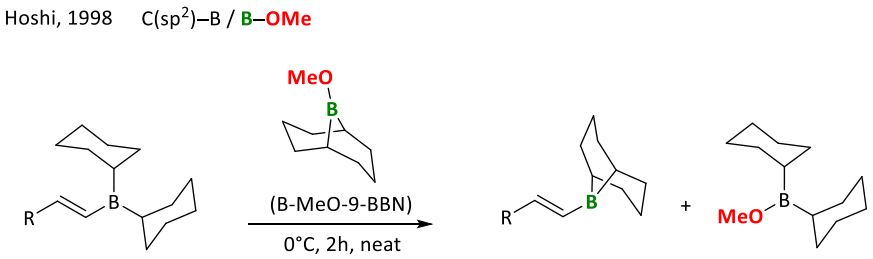
Eventually, palladium-catalyzed Heck coupling of alkenyl boronate with (het)aryl halides, has been disclosed to proceed with high stereoselectivity towards the *E*-stereoselectivity (Scheme 2d).[12] In parallel, the palladium catalyzed Heck reaction between terminal alkenes and catecholchloroborane, ClBcat, represents an alternative procedure.[13]



Scheme 2. Complementary strategies towards *E*-alkenyl boronates.

A new synthetic strategy towards the *E*-alkenyl boronate formation is based on the transborylation pathway. This protocol has been developed recently and the nature of the boryl moiety seems to influence the reactivity and stability of the resulting alkenyl boronate compound.

In 1998, Hoshi and co-workers developed the first example of an alkenyl group transfer from boron to boron in stoichiometric amounts without the presence of metal catalysts.[14] They proved that *E*-alkenyl dicyclohexylborane reacts smoothly at 0 °C with 9-methoxy-9-borabicyclo[3.3.1]nonane (B-MeO-9-BBN) (Scheme 3).This exchange of boryl moieties was performed to be synthetically useful, under mild conditions, with complete retention of configuration through the cleavage of stable boron-oxygen bond in B-MeO-9-BBN.



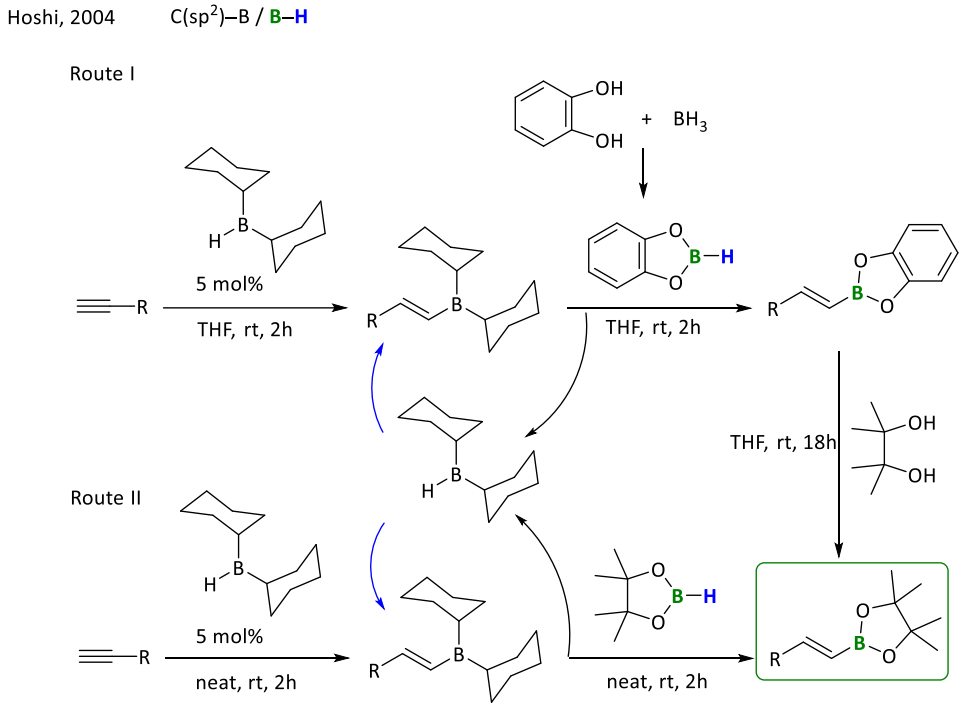
Scheme 3. First example of transborylation by Hoshi and co-workers.

The same authors disclosed later the transfer of the alkenyl group from dicyclohexylborane (BCy_2) to pinacolborane (HBpin) as an alternative methodology to synthesize 1-alkenyl pinacolborane compounds, maintaining the original *E*-stereoselectivity (Scheme 4).[15] They reported two efficient routes to obtain *E*-alkenyl boronic acid pinacol esters.

Route I covers dicyclohexylborane-mediated hydroboration of 1-alkynes with catecholborane in THF followed by transesterification with pinacolborane. This route seems to conduct first the hydroboration of the alkyne, which proceeds under catalytic amount of dialkylborane in THF at room temperature, followed by reaction with catecholborane, generated in situ by the reaction between BH_3 and catechol. This reaction provided the corresponding alkenyl boronic acid catechol ester that was efficiently converted into alkenyl boronic acid pinacol ester by one-pot transesterification reaction with pinacol (Scheme 4, Route I).

On the other hand, the second reported route affords the corresponding hydroborated products in the presence of a catalytic amount of dicyclohexylborane with pinacolborane, under neat conditions at room temperature, in high yields (Scheme 4, Route II). This practical

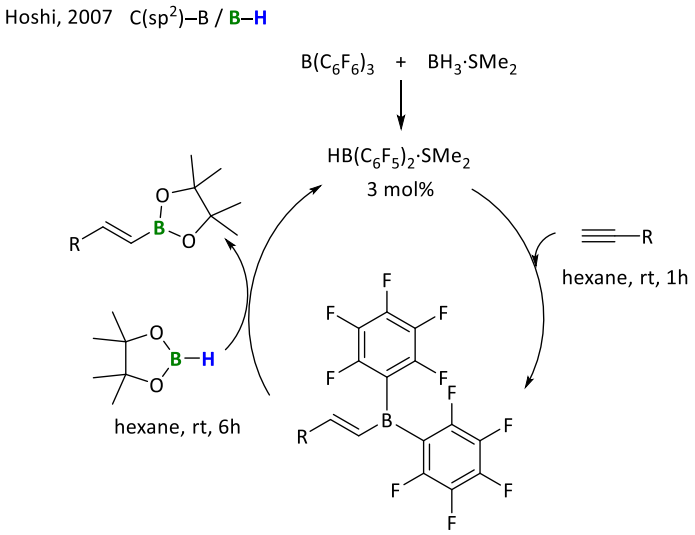
alternative route was extremely efficient to be applied to prepare *E*-alkenyl boronates directly by reaction of HBpin, maintaining the original stereoselectivity.



Scheme 4. Efficient routes to obtain *E*-alkenyl boronic acid pinacol esters by Hoshi and co-workers.

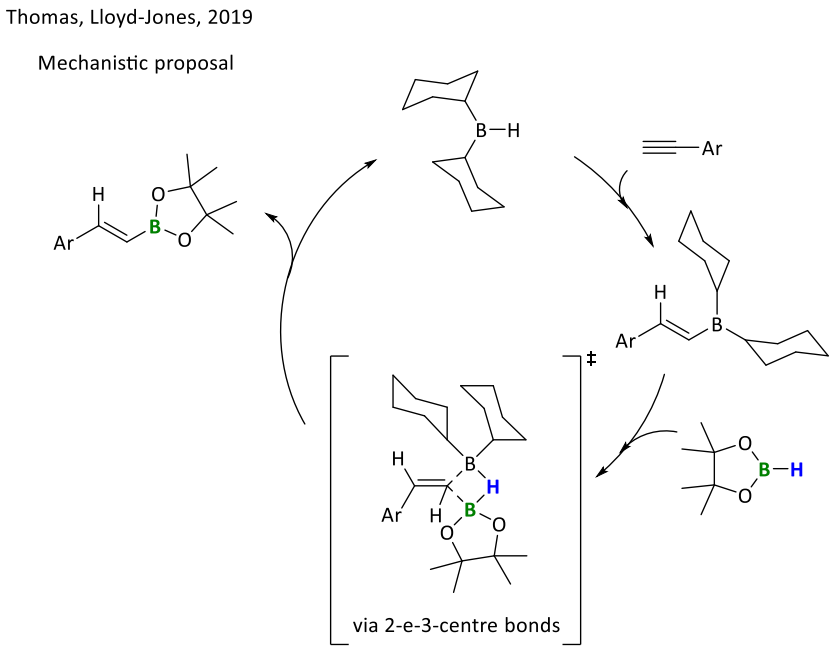
In 2007, Hoshi and co-workers reported the hydroboration reaction between bis-(pentafluorophenyl)borane $(HB(C_6F_5))_2$ and terminal alkynes (Scheme 5).[16] Bis-(pentafluorophenyl)borane is an extremely active hydroborating agent, capable to react at a much faster rate than other hydroborated agents. It can be prepared by a redistribution reaction of tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ and borane-dimethyl sulfide complex $(BH_3{\cdot}SMe_2)$, in hexane, giving the formation of $HB(C_6F_5)_2{\cdot}SMe_2$ as a clear liquid.

Hoshi and co-workers conducted the hydroboration reaction with a wide range of alkyne compounds. In the presence of a catalytic amount of $HB(C_6F_5)_2{\cdot}SMe_2$, generated in situ, the bis(perfluorophenyl)(alkenyl)borane was next transborylated with pinacolborane towards the formation of *E*-alkenyl pinacolboronate with retention of the stereoselectivity.



Scheme 5. Proposal mechanism for $HB(C_6F_5)_2{\cdot}SMe_2$-mediated hydroboration reaction by Hoshi.

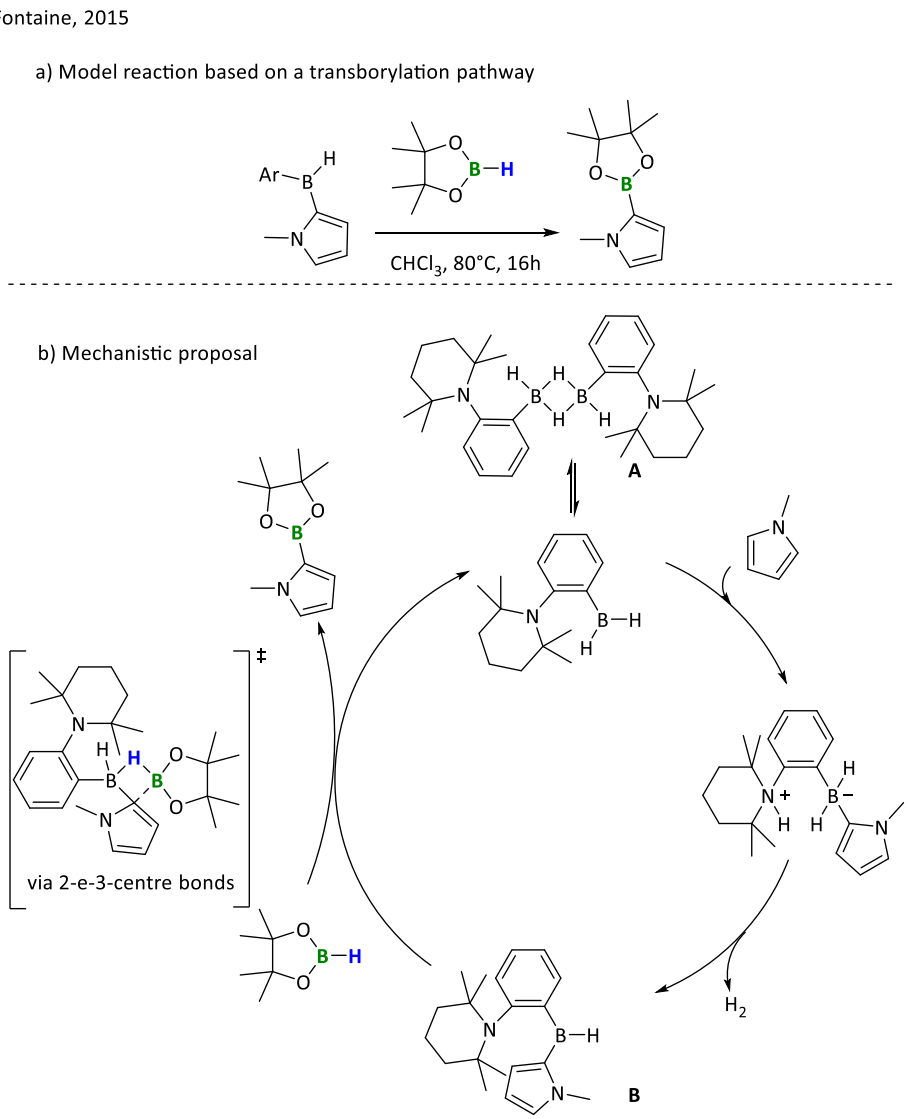
Challenged by the lack of fundamental understanding of these transformations, the mechanism of the transborylation between C(sp^2)−B and B−H has been deeply studied by Thomas, Lloyd-Jones and co-workers.[17] They demonstrated that the key step for the mechanism of R_2BH-catalyzed hydroboration of alkynes is B−H/C−B metathesis, proceeding by stereospecific transfer of the *E*-alkenyl group within a transient, μ−B−H−B bridged, 2-electron-3-center bonded B−C−B intermediate (Scheme 6).



Scheme 6. Mechanistic proposal for transborylation reaction suggested by Thomas and Lloyd-Jones.

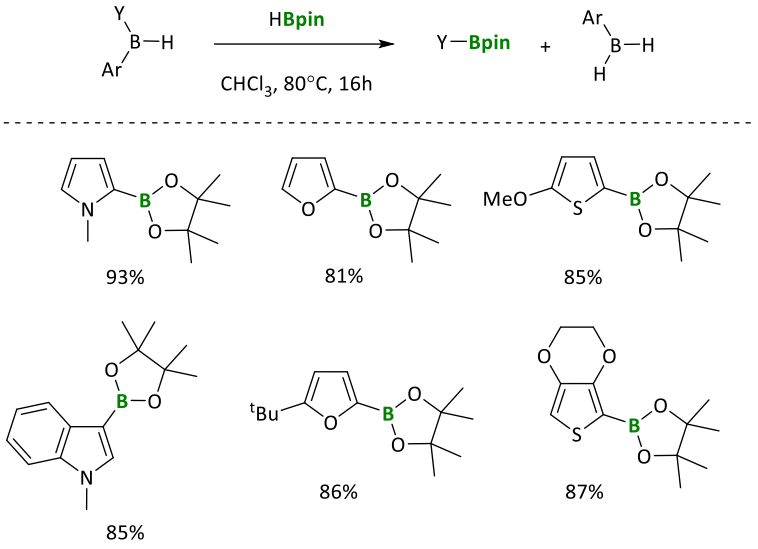
Inspired by those results, they investigated alkyne hydroboration catalyzed by commercially available 9-borabicyclo[3.3.1]nonane dimer $(9\text{-BBN})_2$ instead of air-sensitive $(Cy_2BH)_2$ suspension. The results showed a similar set of intermediates to those found by Hoshi hydroboration reaction; however, the catalyst $(9\text{-BBN})_2$ is more prone to promote secondary hydroboration.

In 2015, Fontaine and co-workers studied the metal-free C–H functionalization of heteroarenes with boranes.[18] They demonstrated that boranes could activate the C−H bonds of heteroarenes by intramolecular frustrated Lewis pair (FPLs) pathway allowing the C−H bond cleavage and subsequent dehydrogenative borylation of heteroarenes without noble metals. This process offers an important breakthrough in the metal-free hydroboration reaction involving low cost and low toxicity of organoboranes. Compound **A** $(TMP\text{-}2\text{-}BH_2\text{-}C_6H_4)_2$ (TMP = 2,2,6,6-tetramethylpiperidine) was the candidate to activate the $C(sp^2)$ −H of the heteroarene (Scheme 7). This catalyst was designed to keep the nucleophilic carbon of the heteroarene close to the Lewis acidic BH_2 moiety. However, the compound was shown to be in equilibrium with the monomeric form which was reported to be the active specie. Based on these experiments, they disclosed the following mechanism for the C−H functionalization of heteroarenes. First, the active specie reacts with 1-methylpyrrole, as the model substrate, generating compound **B** by proton transfer and subsequent borylation reaction (Scheme 7). Finally, the reaction between compound **B** and HBpin might proceed via a 2-electron-3-centre bonds transition state, generating the borylated heteroarene compound and regenerating the $(TMP\text{-}2\text{-}BH_2\text{-}C_6H_4)_2$ specie. With this proposed mechanism in hand, the authors suggested that heteroarene hydroboration proceeds by boryl-exchange metathesis which is the key step of this catalytic cycle.



Scheme 7. Proposed mechanism for the borylation of 1-methylpyrrole with subsequent transborylation.

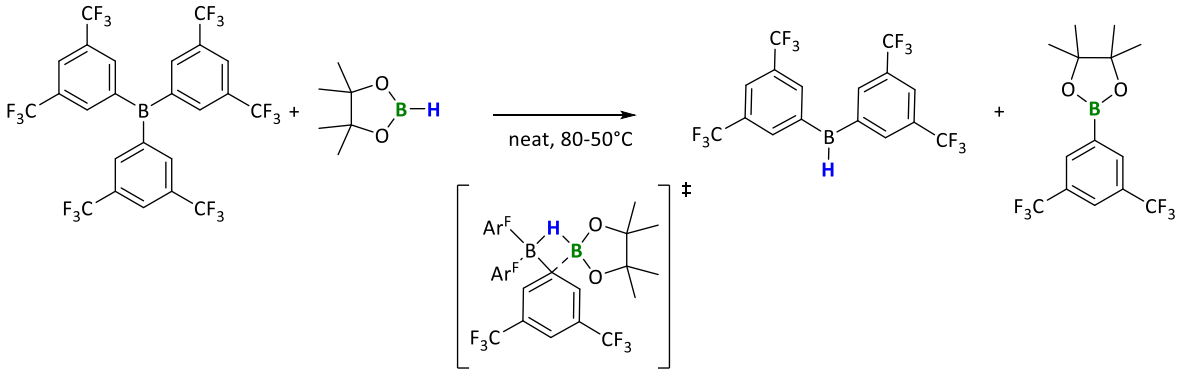
Alternative C(sp^2)−B systems, such as furyl−B, pyrrolyl−B and electron-rich thiophenyl−B, are able to transfer the alkenyl group to HBpin, with the consequent formation of the stable organopinacolborane, via postulated σ-bond metathesis pathway (Scheme 8).



Scheme 8. Substrate scope for transborylation reaction with HBpin.

Oestreich and co-workers[19] observed the transborylation pathway between tris(3,5-bis(trifluoromethyl)phenyl)borane (BAr_3^F) and HBpin (Scheme 9), being the first example of transborylation with aryl groups.

Oestreich, 2016

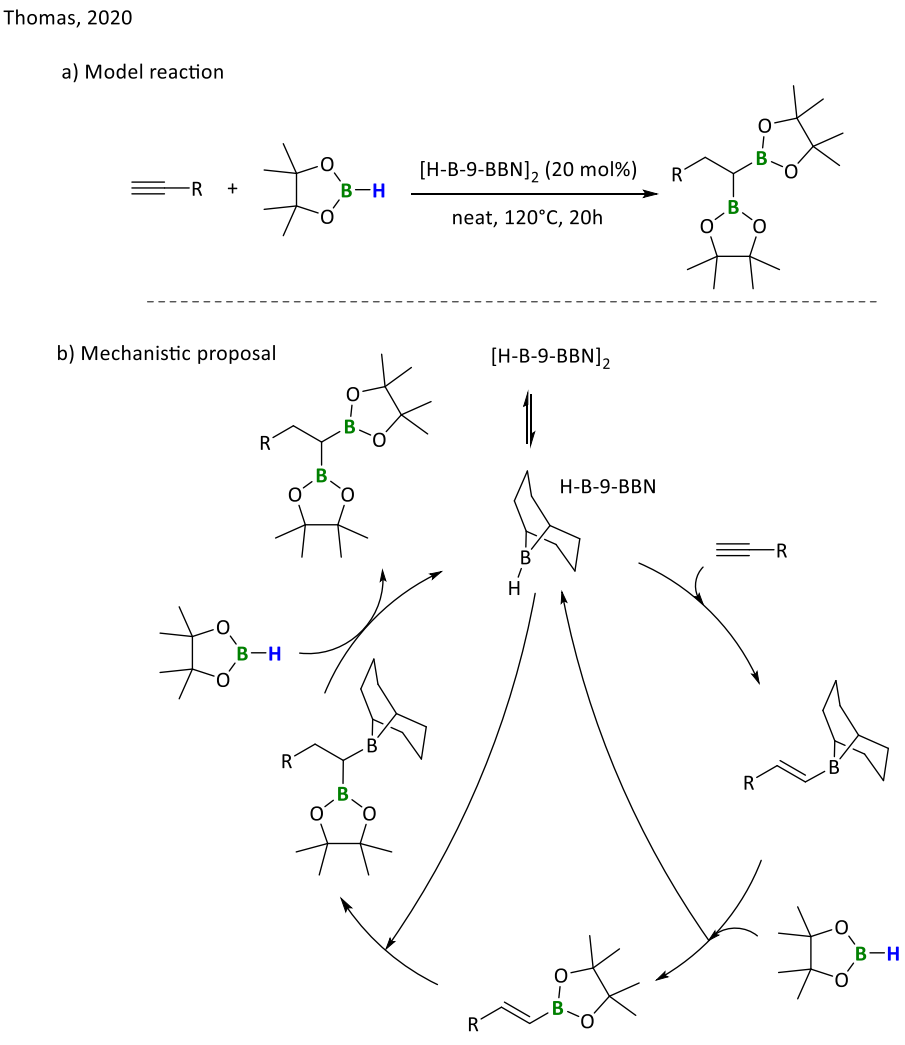


Scheme 9. Transborylation between B–Aryl and HBpin.

More recently, Thomas and co-workers have reported a double transborylation strategy for the synthesis of *gem*-diborylalkanes using reagent 9-borabicyclo[3.3.1]nonane (H-B-9-BBN), as a catalyst and pinacolborane as the transborylative reagent.[20] Their investigations led to a proposal mechanism where borane-catalyzes alkyne hydroboration and subsequent C(sp^3)–B/B–H transborylation reaction gives the versatile and stable *gem*-diboryl alkane compound (Scheme 10).

Commercially available $[H\text{-}B\text{-}9\text{-}BBN]_2$ dimer provides reactive monomeric H-B-9-BBN reagent which is the responsible for alkyne hydroboration reaction generating the

intermediate *E*-alkenyl-B-9-BBN specie (Scheme 10). The second step involves the subsequent formation of *E*-alkenyl pinacol boronic ester and recovery of H-B-9-BBN through C(sp^2)−B/B−H transborylation reaction. Then, *E*-alkenyl pinacol boronic ester and H-B-9-BBN react again to generate intermediate mixed *gem*-diboryl specie through regioselective hydroboration reaction. Finally, C(sp^3)−B/B−H transborylation is afforded giving the desired *gem*-diboryl alkane product and regenerating the monomeric H-B-9-BBN catalyst. The rate-determining step of this catalytic cycle would be the conversion of the intermediate mixed *gem*-diboryl specie (Bpin/B-9-BBN) towards the product *gem*-diboryl alkane (Bpin/Bpin) (Scheme 10).

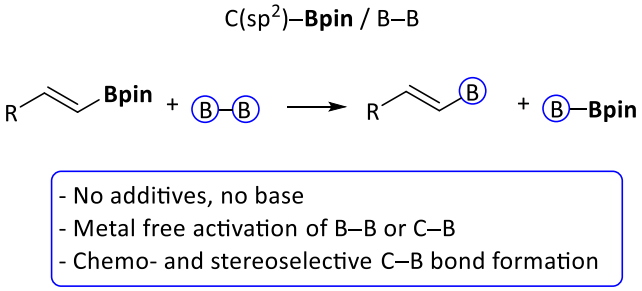


Scheme 10. Proposed mechanism for borane-catalyzed double transborylation.

3. Objectives

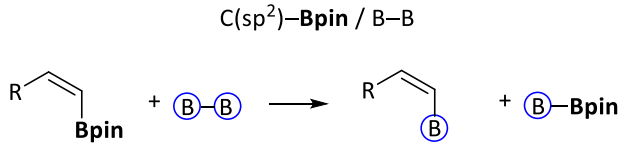
Transborylation reactions, performed so far, have in common that the R group is transferred from very reactive boryl motifs (BCy_2 or $B(C_6F_5)_2$) to pinacolborane (HBpin) via C–BR_2 / H–Bpin metathesis.

The first and main goal of this *Master Thesis* is the study of a new type of transborylation reaction from accessible *E*-alkenyl pinacolborane and symmetric diboron reagents to explore the viability and the driving force for C(sp^2)–**Bpin** / B–B metathesis (Scheme 11).



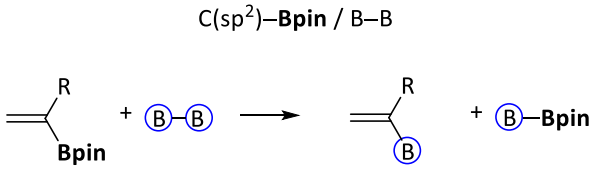
Scheme 11. Work hypothesis for C(sp^2)–Bpin/B–B metathesis.

The second objective is devoted to exploring the transborylation between *Z*-alkenyl pinacolborane compounds and symmetric diboron reagents in order to determine the plausible retention of stereoselectivity (Scheme 12).



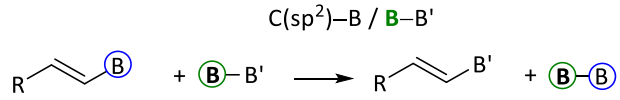
Scheme 12. Work hypothesis for transborylation of *Z*-alkenyl pinacolborane compounds.

The third objective is focused on the transborylation of 1,1-disubstituted alkenyl borane, with the aim to study the compatibility with sterically hindered substrates (Scheme 13).



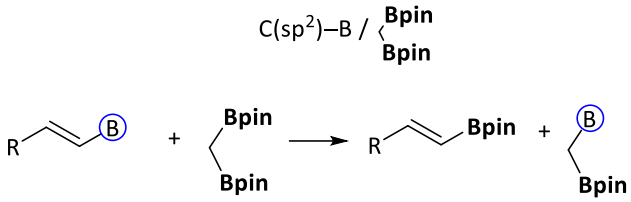
Scheme 13. Work hypothesis for transborylation of 1,1-disubstituted alkenyl borane.

The fourth objective is based on the extrapolation of transborylation reaction between *E*-alkenyl boranes and non-symmetrical diboron reagents (Scheme 14).



Scheme 14. Work hypothesis for transborylation by non-symmetrical reagents.

The fifth objective explores the transborylation reaction between *E*-alkenyl boranes and *gem*-diboryl alkanes with the concomitant formation of non-symmetric *gem*-diboryl alkanes (Scheme 15).



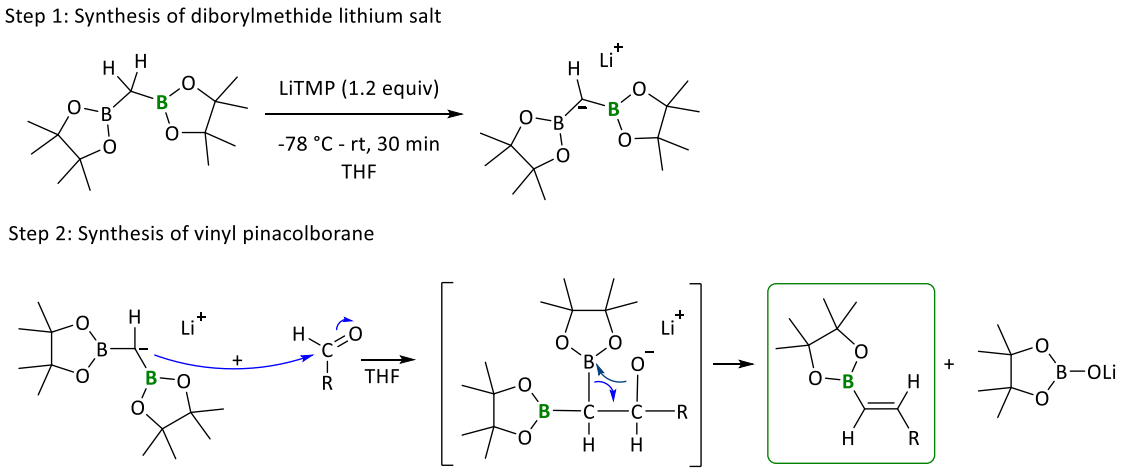
Scheme 15. Work hypothesis for transborylation of symmetric *gem*-diboryl alkanes.

4. Results and Discussion

4.1. Synthesis of alkenyl pinacolboranes

Inspired by these literature precedents, we initiated our studies by synthesizing a series of alkenyl pinacolboranes, through boron-Wittig olefination reaction.[21] The boron-Wittig reaction with *gem*-bis(boryl)alkanes resembles the Wittig olefination based on the formation of alkenes by the condensation of aldehydes or ketones with ylides generated from phosphonium salts. The driving force of Wittig olefination is commonly associated to the formation of a very stable phosphine oxide, whereas in the boron-Wittig transformation the driving force is due to the stability associated to B–O bonds of boronate by-products.

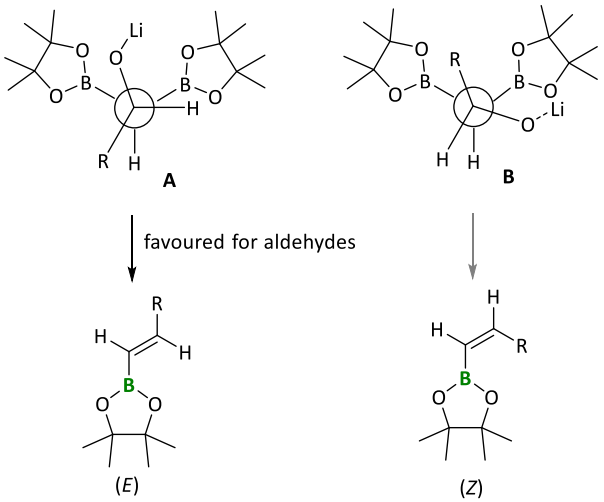
From a mechanistic point of view, boron-Wittig olefination allows the preparation of alkenes by the nucleophilic attack of the α-bis(boryl)carbanions to the carbonyl compound, followed by the attack of oxygen to the Lewis acid forming the tetrasubstituted boronate intermediate, and finally, the formation of the corresponding alkenyl pinacolborane through B–O elimination (Scheme 16).



Scheme 16. Mechanistic sequence of boron-Wittig olefination reaction.

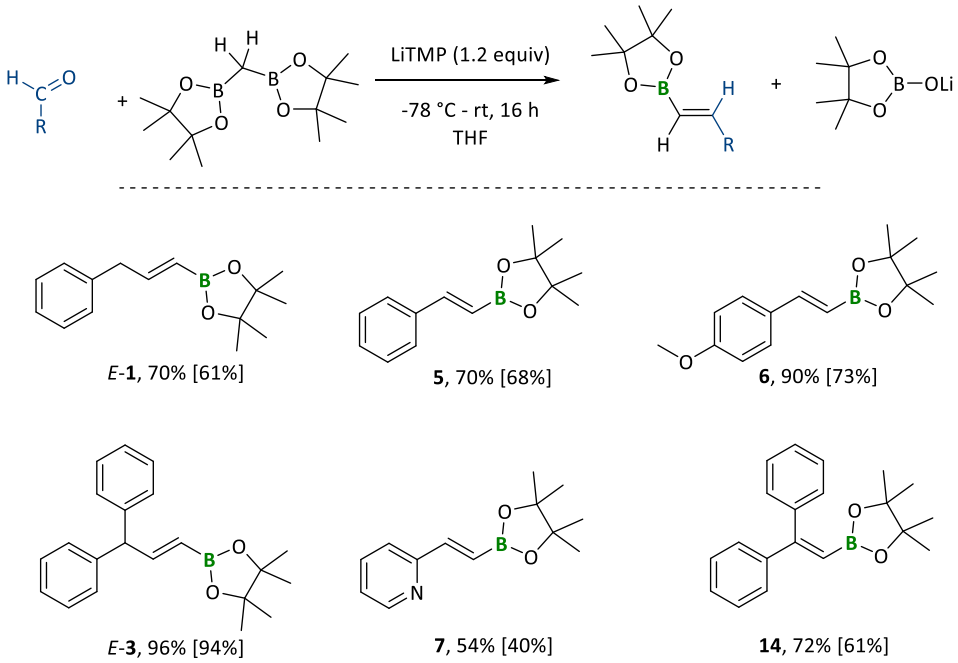
In 2015, Morken and co-workers reported a stereoselective boron-Wittig olefination between bis(pinacolboryl)methane lithium salt and aldehydes,[22] obtaining a variety of synthetically usefull *E*-alkenyl boronate esters. The authors used LiTMP as a base, that was added to $CH_2(Bpin)_2$ at 0 °C, obtaining the diborylmethide lithium salt. The next step was the decrease of temperature to -78 °C followed by the addition of the corresponding aldehyde. Finally, the reaction was stirred for 4 h before being warmed to room temperature. It is worthy to say that Morken and co-workers also observed that similar reaction outcome was conducted when the reaction took place at room temperature (*E*/*Z* ratio 97/3) (Scheme 17).

On the other hand, the same exclusive formation of *E*-alkenyl boronates was observed by Grygorenko and co-workers under the same conditions.[23] The authors justified the control of *E*-stereoselectivity through the conformational models **A** and **B** in Scheme 17. It can be seen that in the case of aldehydes, the conformation **A** might be completely favoured *versus* the conformation **B**.



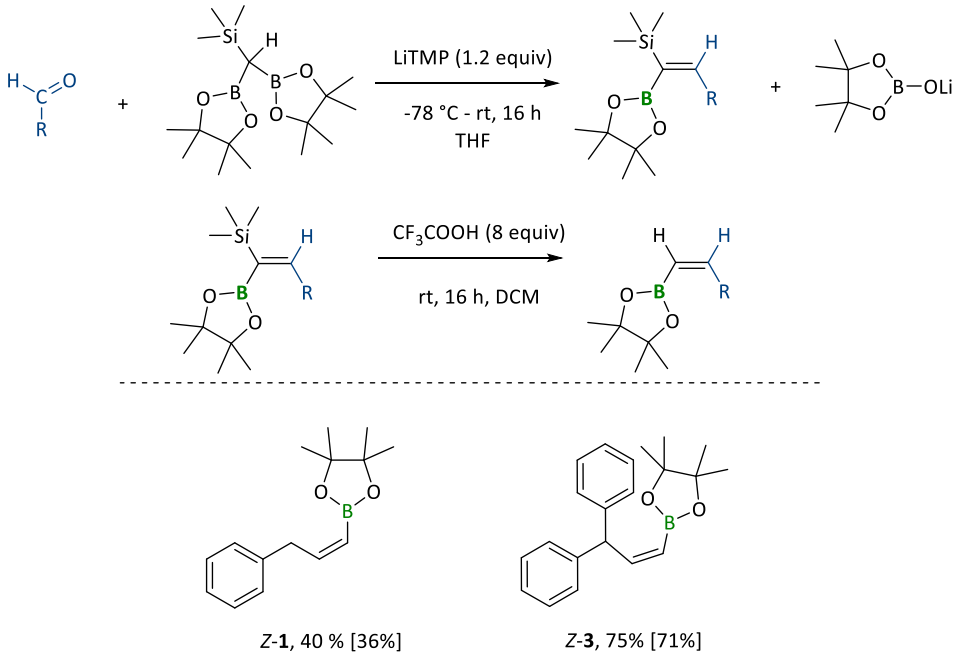
Scheme 17. Suggested models about the origin of the high stereoselectivity in boron-Wittig reaction with aldehydes.

Following this methodology, we have prepared in this work several *E*-1,2-disubstituted boronic esters under the optimized reaction conditions reported in the literature. Yields were moderate for *E*-**1**, **5**, **6**, **7** and **14**, becoming particularly high for compound *E*-**3**. The *E*-isomer was observed preferentially and can be explained due to the total control of *E*-stereoselectivity for the boron-Wittig reaction between aryl aldehydes and $CH_2(Bpin)_2$ in the presence of LiTMP at -78 °C (Scheme 18).



Scheme 18. Substrate scope of *E*-alkenyl pinacolborane compounds.

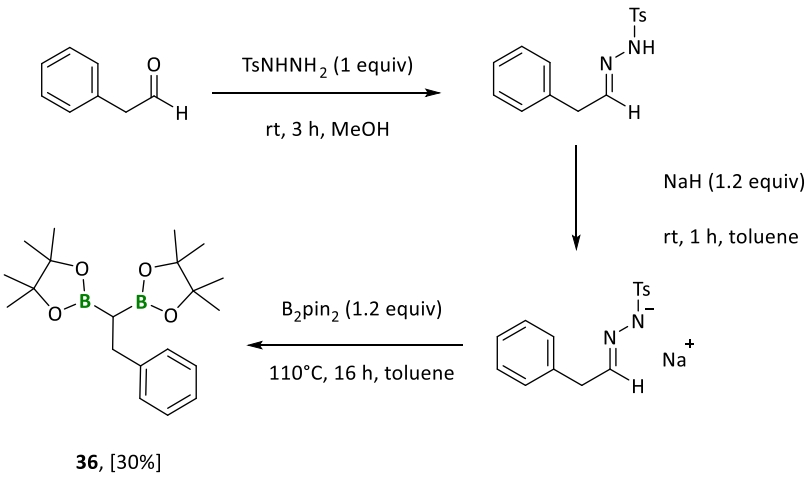
Next, we envisioned the formation of *Z*-alkenyl boranes through boron-Wittig olefination, despite the fact that *Z*-isomers were never obtained in significant ratio. Mimicking the conditions reported by Petit and co-workers,[24] we developed an alternative method via boron-Wittig reaction with (bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane and trifluoroacetic acid. To our delight, we were able to obtain the 1,1-silylboryl alkene with *E*-configuration placing the boryl moiety cis to the R group. Further reaction with CF_3COOH allowed the protodesilylation generating the *Z*-alkenyl pinacolborane as the exclusive alkene.



Scheme 19. Substrate scope of *Z*-alkenyl pinacolboranes compounds.

4.2. Synthesis of *gem*-diboryl alkanes

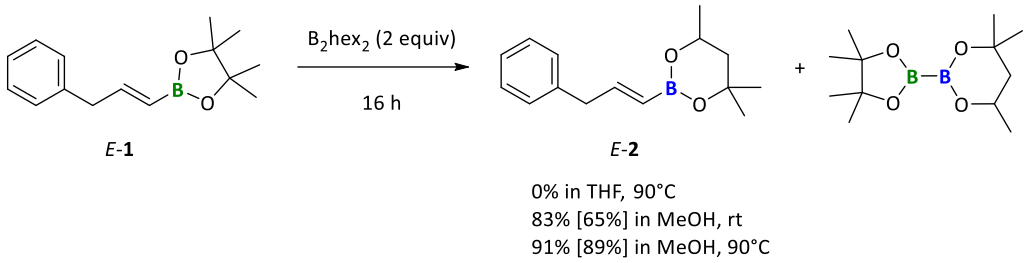
In this work the geminal-diboryl alkane 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **36** has been synthesized from the corresponding sodium tosylhydrazone salt via carbene insertion into bis(pinacolato)diboron (Scheme 20).[25] The first step in this synthesis is the formation of the *N*-tosylhydrazone from the corresponding aldehyde in the presence of $TsNHNH_2$ (1 equivalent). Once it is formed, without isolation, NaH is added to obtain the corresponding sodium tosylhydrazone salt. This kind of salts are precursors of carbenes and working under 110°C the carbene can insert into B_2pin_2 obtaining the corresponding *gem*-diboryl alkane.



Scheme 20. Substrate scope of *gem*-diborylalkanes.

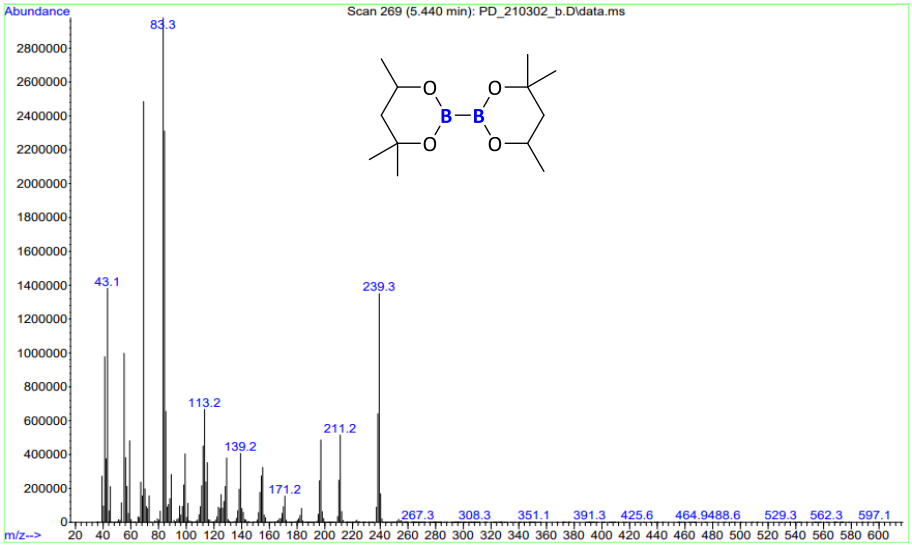
4.3. Study of transborylation of alkenyl pinacolboranes

In this second part of the *Master Thesis,* we turned our attention towards the reactivity of alkenyl pinacolboranes with diboron reagents. To showcase the potential C(sp^2)–Bpin / B–B transborylation reaction, we first evaluated the cross metathesis between *E*-1,2-disubstituted boronic ester *E*-**1** and bis(hexyleneglycolato)diboron (B_2hex_2), at 90°C in THF. This reaction proved to be inefficient since substrate *E*-**1** remained unaltered after 16h of reaction (Scheme 21). Surprisingly, the replacement of THF by MeOH allowed the conversion of *E*-**1** into the alkenyl boronic ester *E*-**2**, from moderate yield at room temperature, to high yield when the reaction was conducted at 90°C. The boronic ester *E*-**2** retained the *E*-configuration from the starting alkenyl pinacolboronate substrate. The mixed diboron reagent pinB–Bhex was formed as a consequence of the Bpin / Bhex exchange. When the crude sample is analyzed by GC-MS, the chromatogram shows the peak of B_2hex_2 (since and excess of reagent is used) as well as pinB–Bhex. Figure 1a and Figure 1b show the mass spectra from the mass spectrometry analysis for B_2hex_2 and pinB–Bhex, respectively.



Scheme 21. Evaluation of C(sp^2)–Bpin / B–B transborylation reaction.

1a)



1b)

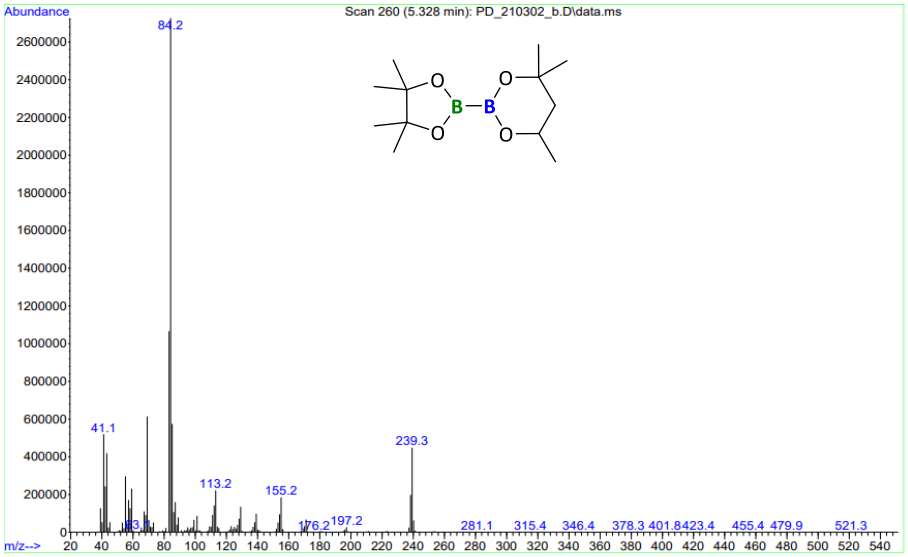
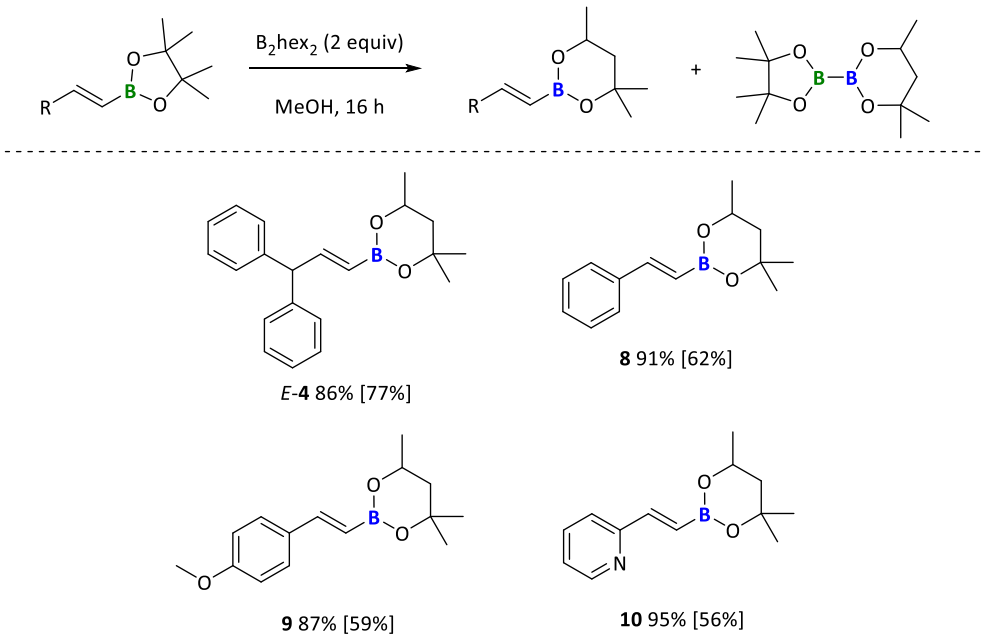
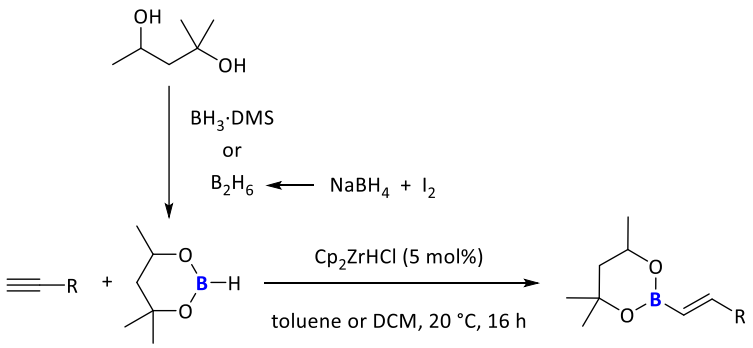


Figure 1. Mass spectra from the MS analysis for 1a) B_2hex_2 and 1b) pinB–Bhex.

We next examined the transborylation of substrates *E*-**3**, **5**, **6** and **7** with B_2hex_2 in MeOH and to our delight the reaction outcome became general for all the substrates tested, forming the corresponding *E*-1,2-disubstituted boronic esters *E*-**4**, **8**, **9** and **10** (Scheme 22). Remarkably, the reaction of substrate **5** in THF, adding 1.5 equivalents of MeOH, only transborylated 9%, confirming the need of MeOH as solvent. This methodology complements the reported synthesis of alkenyl boranes containing Bhex that were prepared before by Cp_2ZrHCl catalyzed hydroboration of terminal alkynes with HBhex. Chavant and co-workers reported that methylpentanediolborane (HBhex) is capable to hydroborate 1-alkynes with Schwart's reagent, as the catalyst, under mild conditions with retention of the configuration (Scheme 23).[26]

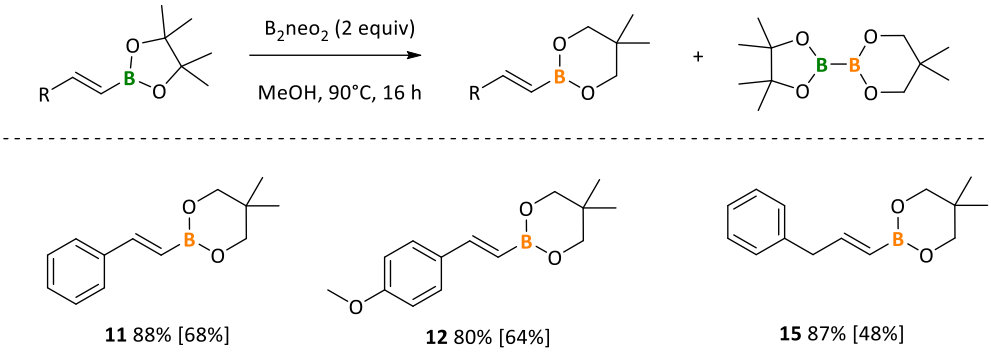


Scheme 22. Substrate scope for transborylation reaction of alkenyl pinacolboranes with B_2hex_2.



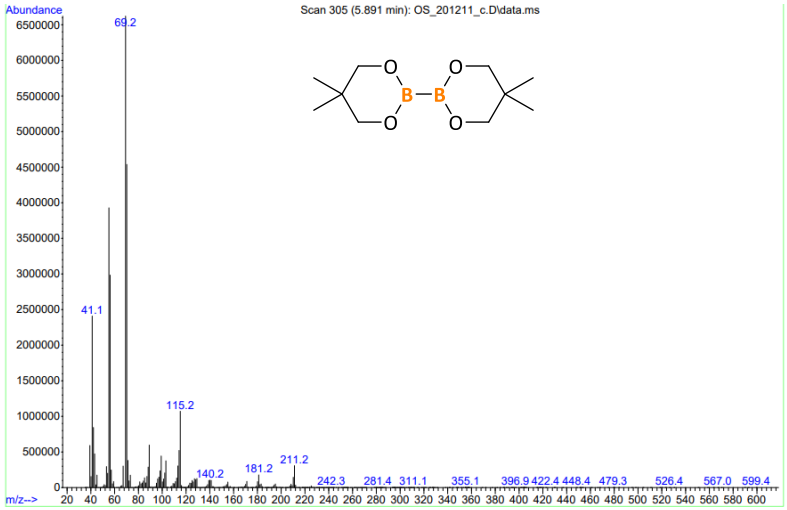
Scheme 23. Hydroboration between 1-alkynes with methylpentanediolborane.

We next explored the transborylation reaction of *E*-**1**, **5**-**6** with bis(neopenthyl glycolato)diboron (B_2neo_2), and the exclusive formation of the transborylated *E*-alkenyl neopentyl glycolato boronic esters **11**-**15** prompted us to assess the generality of this reaction (Scheme 24). The formation of the mixed pinB–Bneo was also observed by GC-MS. Figure 2a and Figure 2b show the spectra of the mass spectrometry analysis for B_2neo_2 and pinB–Bneo, respectively.



Scheme 24. Substrate scope for transborylation reaction of alkenyl pinacolboranes with B_2neo_2.

2a)



2b)

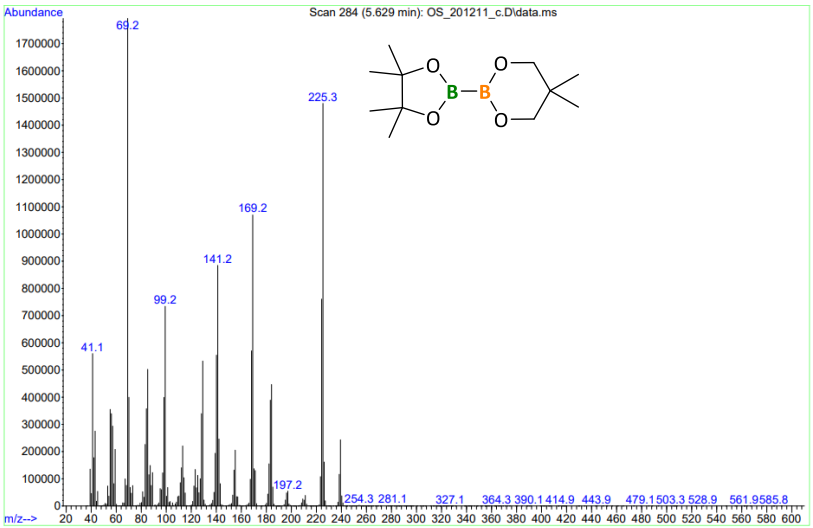
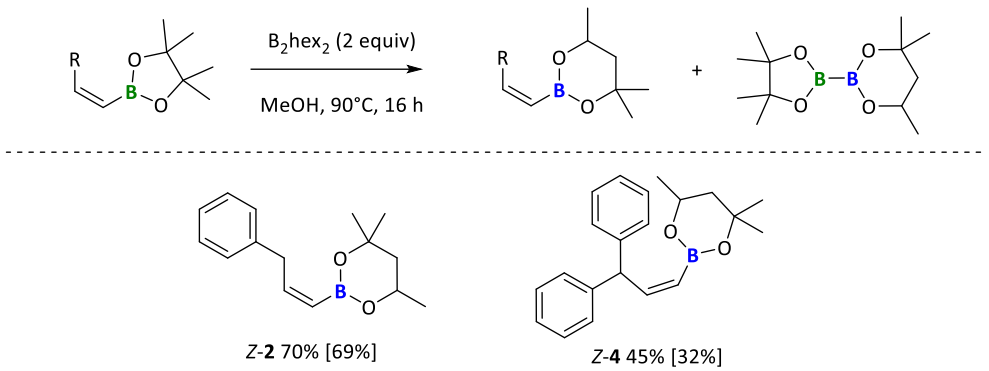


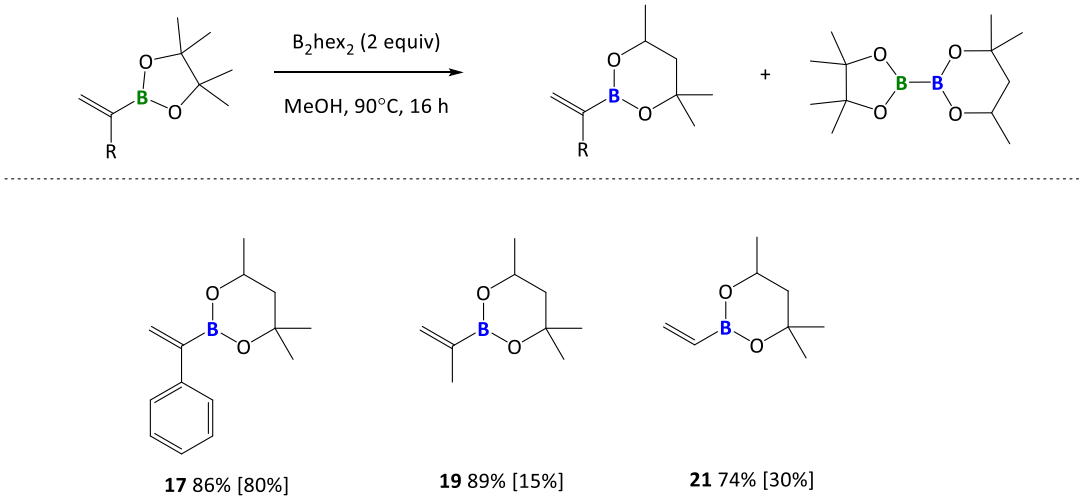
Figure 2. Mass spectra from the MS analysis for 2a) B_2neo_2 and 2b) pinB–Bneo.

Since the configuration of the starting alkenyl pinacolboronate substrate was retained, we next tested the transborylation of *Z*-1,2-disubstituted boronic ester *Z*-**1** and *Z*-**3** with B_2hex_2. Under the optimized reaction conditions, MeOH and 90°C, both substrates were transformed into the corresponding transborylated boronic esters *Z*-**2** and *Z*-**4**, with total retention of the *Z* configuration, although yields were moderate for *Z*-**4**, in comparison with E-**4**, probably due to steric hindrance associated to the *cis* configuration (Scheme 25).



Scheme 25. Substrate scope for transborylation reaction between *Z*-1,2-disubstituted boronic esters and B_2hex_2.

Transborylation of 1,1-disubstituted boronic esters was next studied and substrate **16** was efficiently transborylated with B_2hex_2 in MeOH, isolating 80% of 4,4,6-trimethyl-2-(1-phenylvinyl)-1,3,2-dioxaborinane **17** (Scheme 26). In addition, we were able to perform transborylation of 2-pinacolboryl propene **18** and pinacolboryl ethene **20** into the corresponding transborylated products **19** and **21**, with high conversion, although isolated yield decreased since both products have low boiling points.

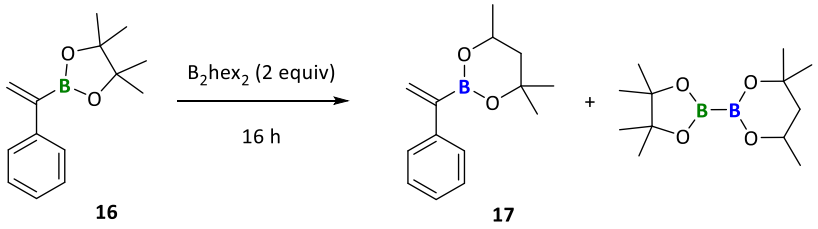


Scheme 26. Substrate scope of B_2hex_2 transborylation reaction of 1,1-disubstituted boronic esters.

4.4. Influence of the solvent

Next, we examined the influence of the solvent in the transborylation reaction. In comparison with substrate **16**, that was efficiently transborylated with B_2hex_2 in MeOH, isolating 80% of product **17**, we performed the reaction under a range of solvents.

Similar reaction outcome was observed using EtOH as solvent, although alternative solvents, such as ^{i}PrOH resulted less efficient for the transborylation (Table 1). In order to survey whether the acidic properties of the solvent had some benefits in the reaction outcome, we considered the use of polyfluorinated alcohols, such as CF_3CH_2OH and $(CF_3)_2CHOH$ (HFIP has particular physical and chemical properties that facilitate unique modes of reactivity and make it an exceptional solvent),[26] however product **17** was only produced in 12% and 16% conversion, respectively. As we have already pointed out, the use of THF as solvent inhibited the transborylation reaction, unless 2 equivalents of LiOMe were added to the reaction media, making possible the transborylation from **16** into **17**, although in lower yields in comparison to the use of MeOH as solvent (Table 1).



Solvent	Yield on 17
MeOH	86% [80%]
EtOH	80%
CF_3CH_2OH	12%
^{i}PrOH	9%
$(CF_3)_3COH$	16%
THF	0%
THF + LiOMe (2 equiv)	74% [42%]

Table 1. Study of the influence of alternative solvents in transborylation of substrate **16** with B_2hex_2. (Yields calculated by ^{1}H-NMR with naphthalene as internal standard. Values in brackets are isolated yields.)

4.5. In-situ ^{1}H-NMR and ^{11}B-NMR spectroscopy studies

Generalizing the use of MeOH as the appropriate solvent, an *in-situ* NMR spectroscopy study on the evolution of the reactivity between **16** and 2 equivalents of B_2hex_2, in CD_3OD, was investigated. Figure 3 shows the evolution of the ^{1}H-NMR spectra along the reaction, illustrating that the new signals associated to the transborylated product **17** appeared after 3h at 90 °C. Within 16h the new alkenyl borane **17** became the predominant species, as it can be seen in the ^{1}H-NMR spectra (Figure 3). On the other hand, parallel *in-situ* ^{11}B-NMR spectroscopy study was conducted along the reaction (Figure 4). Remarkably, more detailed resolution of the boron signals is afforded under elevated NMR temperatures. Based on these results, it can be seen two signals about 18 ppm suggesting that the transborylation reaction proceed via the formation of $R_2B–OCD_3$.

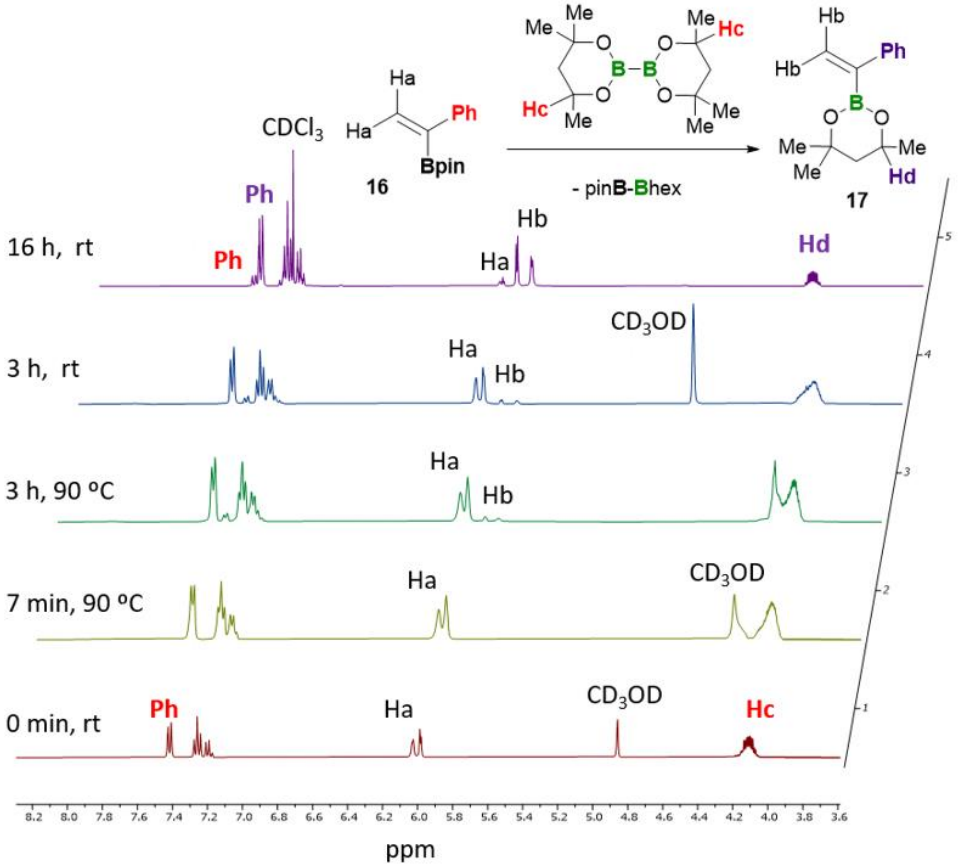


Figure 3. Evolution of the ^{1}H-NMR spectra along the reaction between 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**16**) and B_2hex_2.

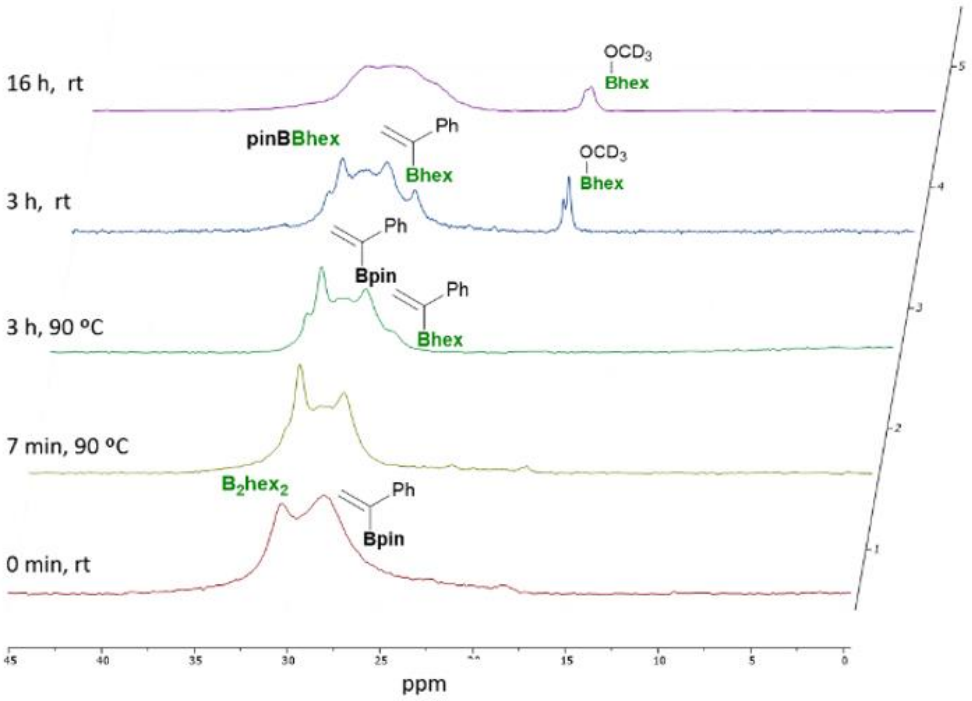
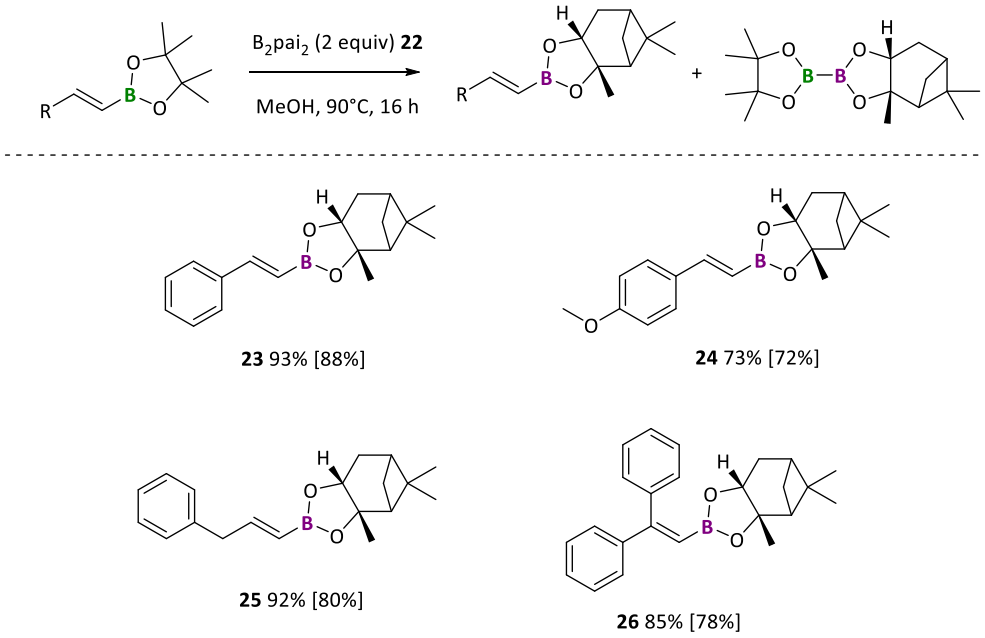


Figure 4. Evolution of the ^{11}B-NMR spectra along the reaction between 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**16**) and B_2hex_2.

4.6. Study of transborylation reaction with chiral diboron reagents

The transborylation with chiral diborane reagents has been accomplished through representative 1,2-disubstituted alkenyl pinacolboronic esters and bis-(+)-pinanediolato diboron (B_2pai_2) (**22**). As a consequence of the cross-metathesis, the mixed pinB–Bpai has been identified as by-product in the reaction mixture (Figure 5). The *E*-configuration has been preserved from the substrates *E*-**1**, **5** and **6** to the chiral alkenyl boranes **23**-**25**, respectively (Scheme 27). Some of those chiral alkenyl boranes were prepared before through hydroboration of terminal alkynes with the chiral 1,3,2-dioxaborolane HBpai.[28] From substrate **14**, the transborylation with B_2pai_2 was also performed efficiently, despite the fact of the steric hindrance (Scheme 27).



Scheme 27. Substrate scope of chiral alkenyl boranes compounds.

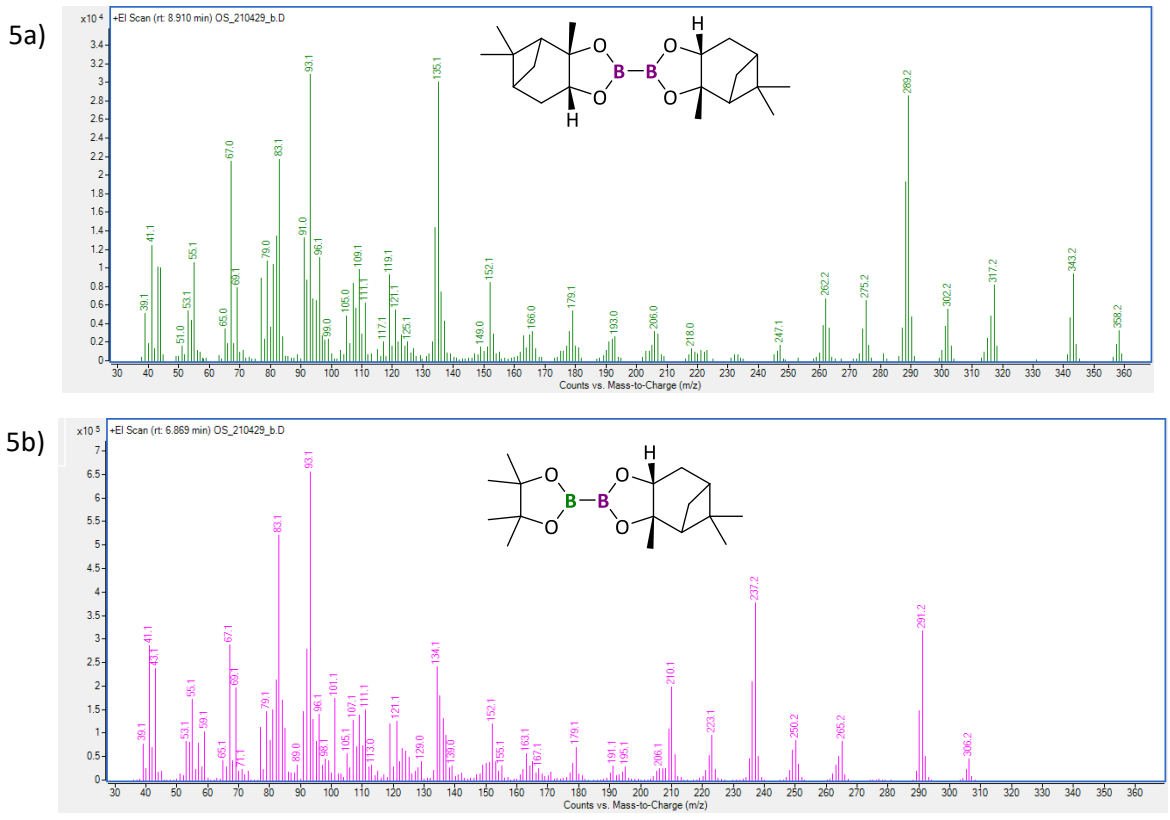
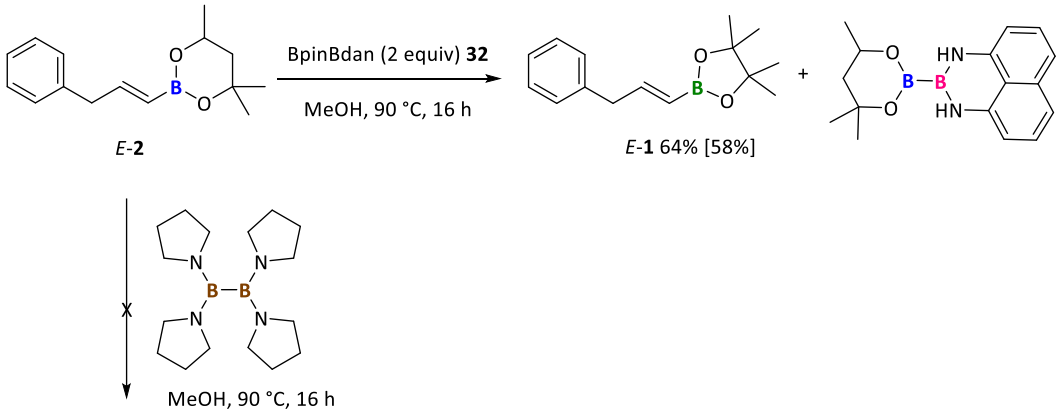


Figure 5. Mass spectra from the MS analysis for 5a) B_2pai_2 and 5b) pinB–Bpai.

4.7. Study about chemoselectivity on transborylation reaction

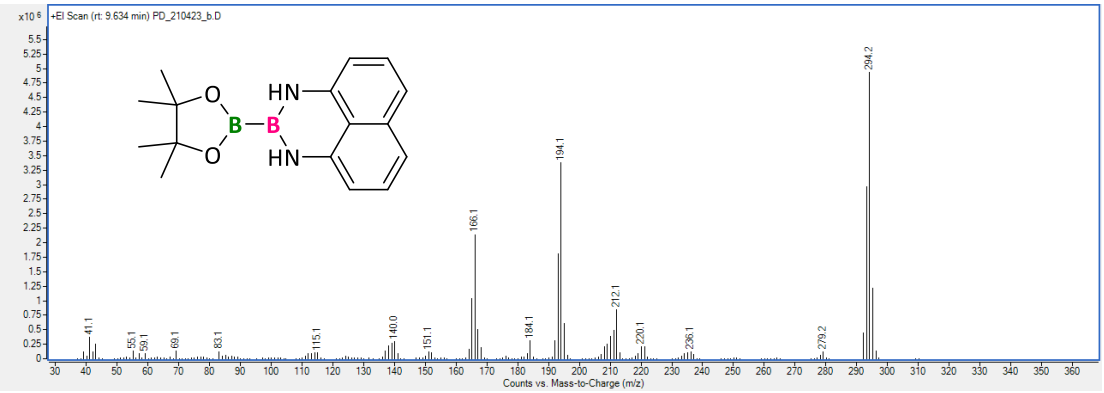
Since our experimental data demonstrate that the symmetrical diboron reagents can be transborylated to the alkenyl pinacolboronic ester substrates, we investigated the effect of other unsymmetrical diboron reagents.

Interestingly, when mixed diboron reagent Bpin-Bdan (**32**) (dan=1,8-diaminonaphthalene) was added to alkenyl boronic ester *E*-**2**, in MeOH, the new C(sp^2)–B bond is produced with the most Lewis acidic boryl moiety, Bpin, generating product *E*-**1** in 58% yield (Scheme 28). As a consequence of this selective cross metathesis, the mixed Bhex–Bdan was identified as the by-product (Figure 6). This transborylation reaction did not proceed in THF, even at 90°C. Another intriguing fact is that alkenyl boronic ester *E*-**2** did not transborylate with tetramino diboron reagent, under the optimized reaction conditions, suggesting that the tetramino diboron could not be activated to promote the cross-metathesis.



Scheme 28. Chemoselective transborylation reactions between *E*-alkenyl boronic ester **2** and Bpin–Bdan.

6a)



6b)

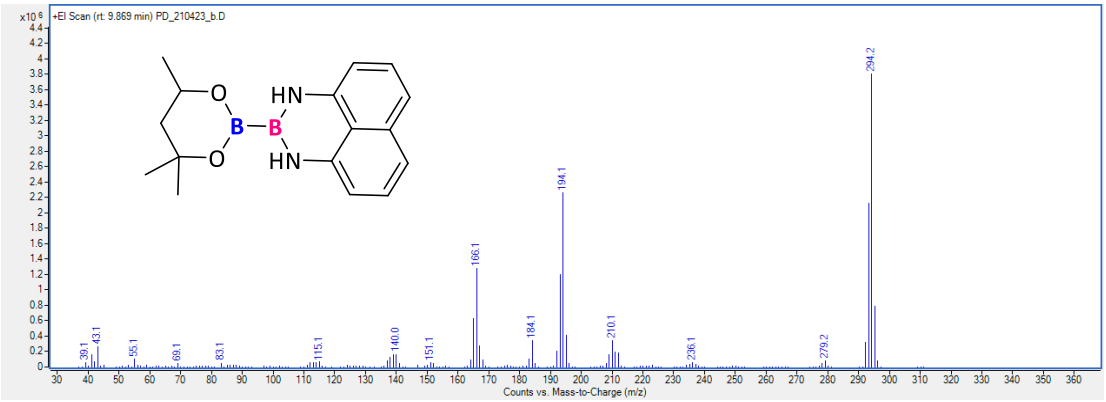
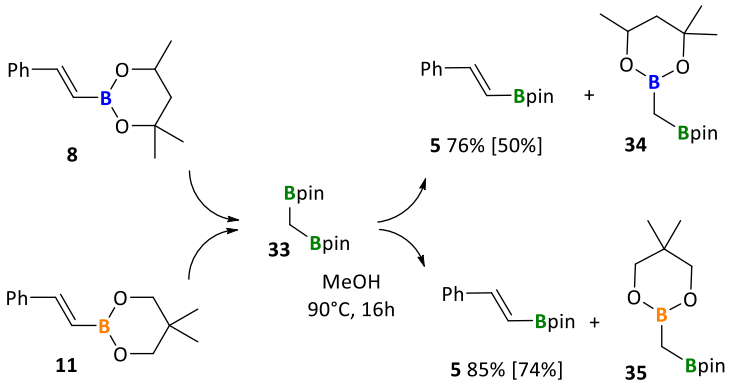


Figure 6. Mass spectra from the MS analysis for 6a) pinB–Bdan and 6b) hexB–Bdan.

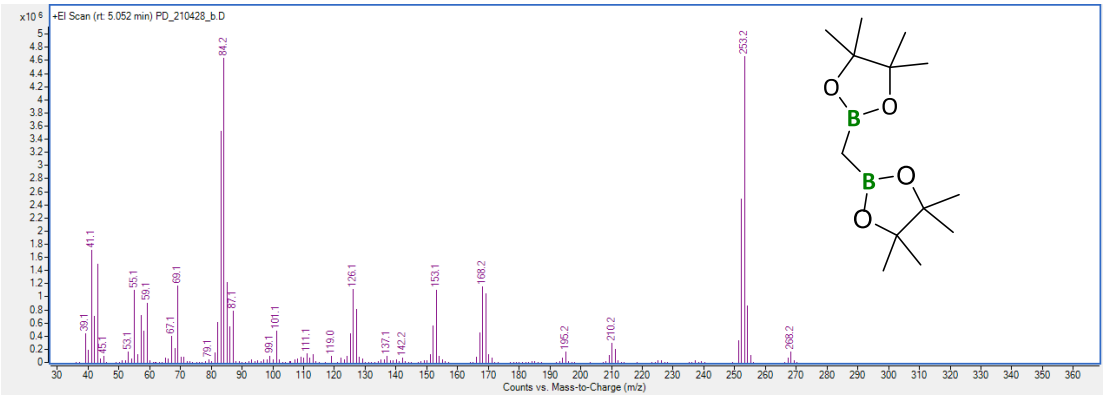
4.8. Transborylation sequence with *gem*-diboryl alkane reagents

Finally, we studied the transborylation sequence between C(sp^2)–B and *gem*-diborylalkane reagents, in an attempt to disclose whether B–C–B can be capable to perform the cross-metathesis. As model reactions we explored the transborylation between *E*-alkenyl boranes **8** or **11** with bis(pinacolboryl)methane (**33**), and to our delight the expected *E*-alkenyl pinacolborane **5** was formed together with the geminal mixed diborylmethane products **34** and **35** (Scheme 29). Figure 7 shows the spectra of the bis(pinacolboryl)methane (**33**) as well as the spectra for the mixed diboryl alkanes **34** and **35**.

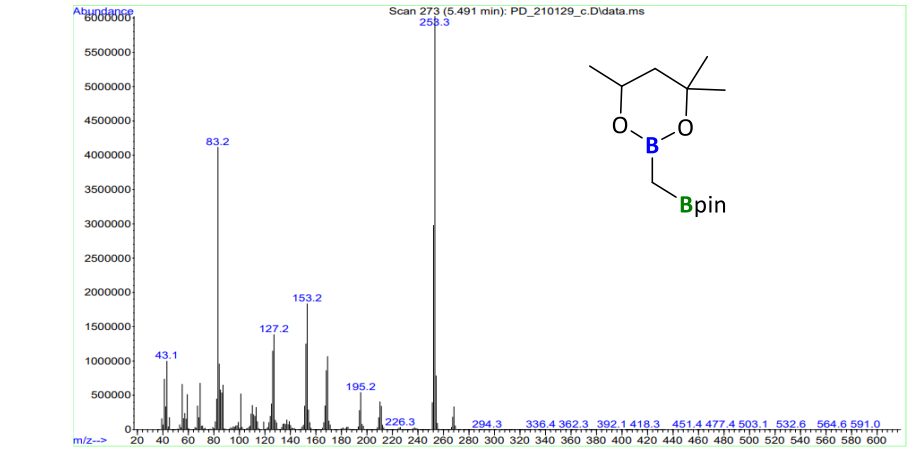


Scheme 29. Transborylation sequence between C(sp^2)–B and *gem*-diboryl alkane reagents.

7a)



7b)



7c)

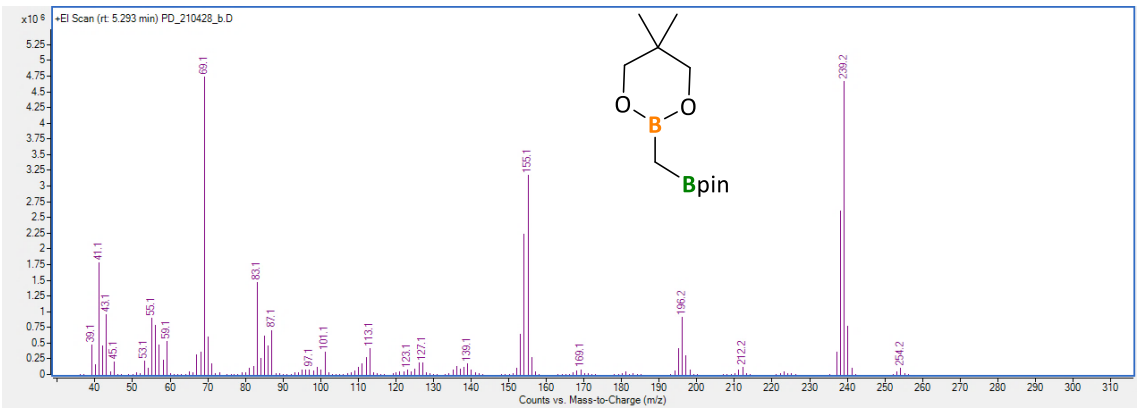
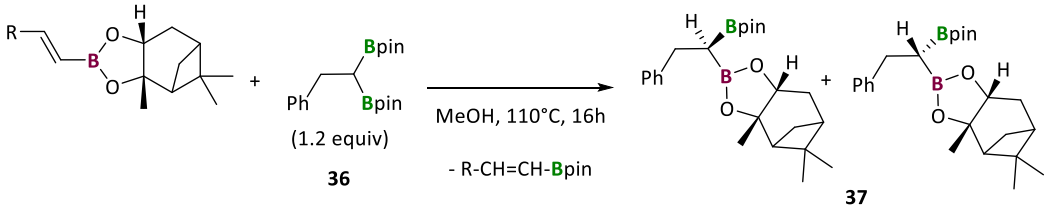


Figure 7. Mass spectra from the MS analysis for 7a) bis(pinacolboryl)methane (**33**) and the mixed diboryl alkanes 7b) **34** and 7c) **35**.

When the chiral alkenyl boranes **23**-**26** reacted with the substituted gem-bis(pinacolboryl) alkane **36**, the cross-metathesis generated the mixed *gem*-(Bpin)(Bpai) alkane **37**, in isolated yields 28-39%, as a mixture of both diastereoisomers (Scheme 30). MeOH seems to be, once again, the solvent of choice, since the transborylation in THF did not proceed. To the best of our knowledge, this is the first transborylation reaction through chiral boryl units, that opens a new opportunity to explore diastereoselection in the synthesis of geminal diborylalkane species.



[28%] d.r.=1:1 from **23**
[38%] d.r.=1:1 from **24**
[39%] d.r.=1:1 from **25**
[28%] d.r.=1:1 from **26**

Scheme 30. Transborylation between chiral *E*-alkenyl boranes and *gem*-bis(pinacolboryl) alkane **36**.

5. Conclusions

The studies in this *Master Thesis* were aimed at investigating a new methodology of transborylation reaction between diboron reagents and alkenyl boranes via C(sp^2)–Bpin / B–B cross-metathesis. It is important to mention that the objectives planned for this work have been accomplished, and the main conclusions are as follow:

- The viability and robustness of the new type of transborylation reaction has been demonstrated.
- We have applied the transborylation reaction for accessing alkenyl boranes with *Z*- and *E*-configuration because of the retention of configuration.
- Additionally, the scope of alkenyl borane complexes has been expanded with the formation of new alkenyl boranes which contain chiral boryl units.
- The study of the reactivity between *E*-alkenyl boranes and unsymmetrical diboron reagents, suggests that transborylation reaction undergoes through the most Lewis acidic boryl moiety.
- Synthesis of unsymmetrical *gem*-diboryl alkanes through transborylation between *E*-alkenyl boranes and *gem*-diboryl alkanes, has been accomplished being the first example of transborylation with geminal diboron compounds.

Additional studies concerned to the mechanistic insights have been developed in collaboration with Dr. Jordi Carbó and Mr. Gerard Bru, from the University Rovira i Virgili.

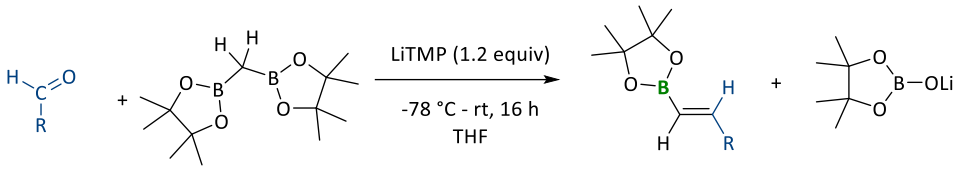
6. Experimental section

6.1. Materials and Methods

Solvents and reagents: Solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl. Lithium 2,2,6,6-tetramethylpiperidide and vinyl boranes **16**, **18** and **20**, were purchased from Sigma-Aldrich Inc. Diboron reagents were purchased from Ally Chem and used without further purification. All reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon, using Schlenk-type techniques. Flash chromatography was performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Thin layer chromatography was performed on Merck Kieselgel 60 F254 which was developed using standard visualizing agents: UV fluorescence (254 and 366 nm) or potassium permanganate/Δ. NMR spectra were recorded at a Varian Goku 400 or a Varian Mercury 400 spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm (^{1}H)) and ($CDCl_3$: 77.16 ppm (^{13}C). $^{11}B\{^{1}H\}$ NMR chemical shifts (δ) are reported in ppm relative to $(CH_3)_2O\cdots BF_3$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptuplet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface and it was performed at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona). GC-MS analyses were performed on a HP6890 gas chromatograph and an Agilent Technologies 5973 Mass selective detector (Waldbronn, Germany) equipped with an achiral capillary column HP-5 (30m, 0.25mm i. d., 0.25µm thickness) using He as the carrier gas.

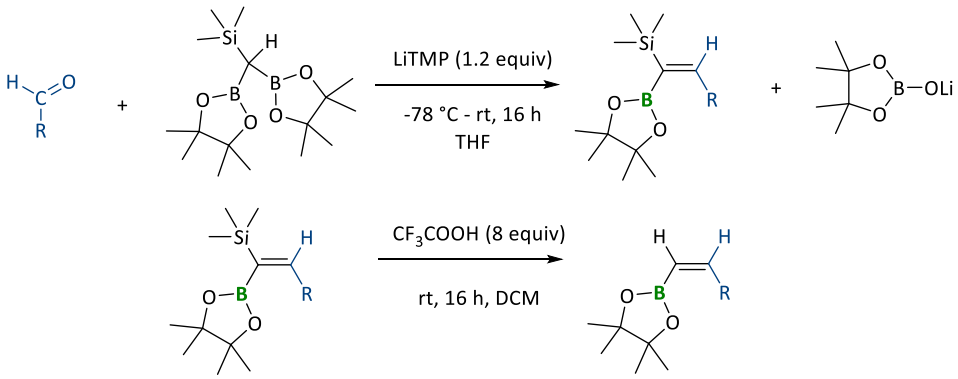
6.2. General procedures

6.2.1. General procedure for the preparation of boron-Wittig *E*-alkenyl pinacolboranes



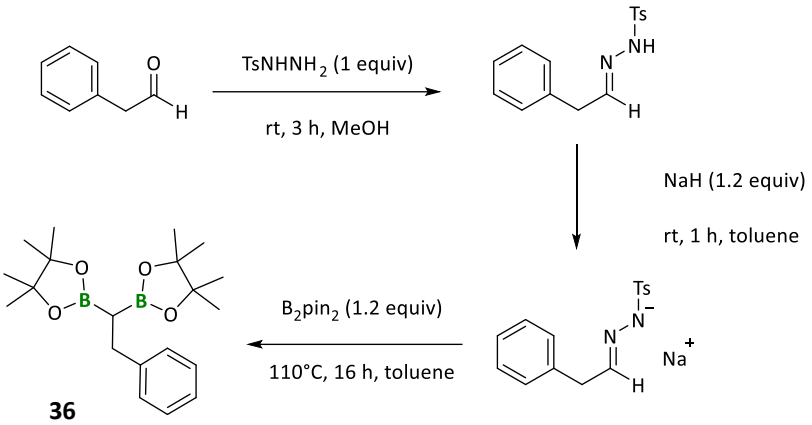
A Schlenk-tube equipped with a magnetic stir bar was charged with *geminal*-diboryl alkanes (0.5 mmol, 1 equiv) and LiTMP (0.6 mmol, 1.2 equiv) in dry THF as solvent (2 mL). The mixture was stirred during 30 min at 0 °C. Then, the aldehyde (0.8 mmol, 1.6 equiv) was added. The reaction was stirred during 10 min at 0 °C, followed by 16 h at room temperature. The solvent was gently concentrated at the rotary evaporator and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

6.2.2. General procedure for the preparation of boron-Wittig *Z*-alkenyl pinacolboranes



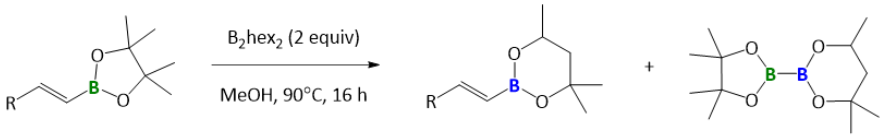
A Schlenk-tube equipped with a magnetic stir bar was charged with *geminal*-diboryl alkanes (0.5 mmol, 1 equiv) and LiTMP (0.6 mmol, 1.2 equiv) in dry THF as solvent (2 mL). The mixture was stirred during 30 min at 0 °C. Then, the aldehyde (0.8 mmol, 1.6 equiv) was added. The reaction was stirred during 10 min at 0 °C, followed by 16 h at room temperature. The solvent was gently concentrated at the Schlenk line. Next, 3 mL of dry dichloromethane and CF_3COOH (3 mmol, 8 equiv) were added and the reaction was stirred for 16 h at room temperature. The solvent was gently concentrated at the rotary evaporator and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

6.2.3. General procedure for the preparation of 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (36)



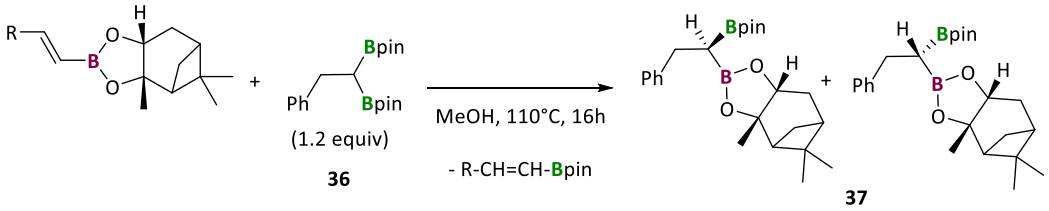
Tosylhydrazine (14.4 mmol, 1.2 equiv.) was dissolved in methanol (30mL) in a Schlenk flask. Then, a solution of 2-phenylacetaldehyde (12 mmol, 1 equiv.) in MeOH was added to the solution of tosylhydrazine and the mixed solution was stirred for 3h. The reaction was followed by TLC analysis. When the aldehyde spot disappeared, methanol was removed. The obtained N-tosylhydrazone was reacted with NaH (60%) in 80 mL of dry toluene and it was stirred for 1 h at room temperature. Then, B_2pin_2 (14.4 mmol, 1.2 equiv.) was added with additional 5mL of dry toluene and the mixture was stirred for 16h at 110 °C. The reaction mixture was cooled down to room temperature and the obtained suspension was filtered through Celite® and the solvent was evaporated on a rotatory evaporator. Subsequently, the crude was purified by silica gel flash chromatography to afford the geminal-diboryl alkane.

6.2.4. General procedure for transborylation of alkenyl pinacolboranes



A Schlenk-tube equipped with a magnetic stir bar was charged with boron-Wittig product (0.3 mmol, 1 equiv), diboron reagent (0.6 mmol, 2 equiv) in dry MeOH as solvent (2 mL). The mixture was stirred during 16 h at 90 °C. The solvent was gently concentrated at the rotary evaporator and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

6.2.5. General procedure for transborylation with *gem*-diboryl alkanes

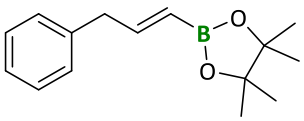


A Schlenk-tube equipped with a magnetic stir bar was charged with alkenyl borane product (0.6 mmol, 1.2 equiv), *gem*-diboryl alkane product (0.5 mmol, 1 equiv) in dry MeOH as solvent (4 mL). The mixture was stirred during 16 h at 110 °C. The solvent was gently concentrated at the rotary evaporator and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

6.3. Spectral data for alkenyl boranes

6.3.1. Spectral data for boron-Wittig *E*-alkenyl pinacolboranes

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*E*-1)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *E*-**1** (61%, 75 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 – 7.13 (m, 2H), 7.15 – 7.04 (m, 3H), 6.68 (dt, J = 17.8, 6.3 Hz, 1H), 5.37 (dt, J = 17.8, 1.7 Hz, 1H), 3.39 (dd, J = 6.3, 1.7 Hz, 2H), 1.16 (s, 12H).

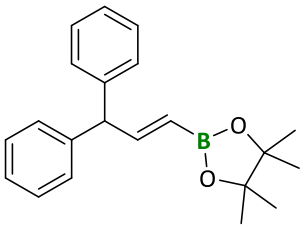
^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.47, 139.10, 128.95, 128.46, 126.18, 83.12, 42.30, 24.82.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.58.

These data are in agreement with those reported in the literature.[29]

HRMS (ESI) for **$C_{15}H_{21}BO_2$ [M+NH_4^+]$^+$:** calculated: 262.1979, found: 262.1978.

(*E*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*E*-3)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *E*-**3** (94%, 110 mg) as a pale yellowish oil.

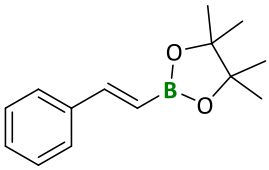
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.25 (m, 5H), 7.23 – 7.16 (m, 5H), 7.05 (dd, J = 17.9, 6.9 Hz, 1H), 5.40 (dd, J = 17.9, 1.5 Hz, 1H), 4.82 – 4.76 (m, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.58, 142.65, 130.07, 128.80, 128.40, 126.42, 83.20, 56.86, 24.82.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.23.

HRMS (ESI) for **$C_{21}H_{25}BO_2$ [M+NH_4^+]$^+$:** calculated: 338.2291, found: 338.2299.

(*E*)-4,4,5,5-Tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (5)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **5** (68%, 66 mg) as a pale yellowish oil.

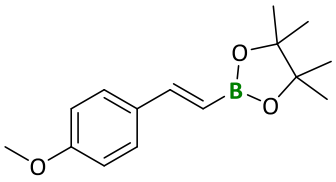
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.45 (m, 2H), 7.40 (d, J = 18.5 Hz, 1H), 7.38 – 7.26 (m, 3H), 6.17 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.52, 128.90, 128.58, 127.07, 83.37, 24.83.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.16.

HRMS (ESI) for **$C_{14}H_{19}BO_2$ [M+H^+]$^+$:** calculated: 231.1556, found: 231.1555.

(*E*)-4,4,5,5-Tetramethyl-2-(4-methoxystyryl)-1,3,2-dioxaborolane (6)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **6** (73%, 80 mg) as a pale yellowish oil.

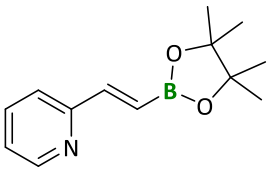
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.34 (m, 2H), 7.28 (d, J = 18.4 Hz, 1H), 6.83 – 6.77 (m, 2H), 5.94 (d, J = 18.4 Hz, 1H), 3.75 (s, 3H), 1.24 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.30, 149.07, 130.42, 128.48, 113.98, 113.33, 83.23, 55.30, 24.82.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.21.

HRMS (ESI) for **$C_{15}H_{21}BO_3$ [M+H^+]$^+$:** calculated: 261.1662, found: 261.1667.

(*E*)-2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (7)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **7** (40%, 37 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (dd, J = 4.8, 1.8 Hz, 1H), 7.65 (dt, J = 7.7, 1.8 Hz, 1H), 7.45 (d, J = 18.3 Hz, 1H), 7.40 (dt, J = 7.9, 1.1 Hz, 1H), 7.17 (dd, J = 7.5, 4.8 Hz, 1H), 6.63 (d, J = 18.3 Hz, 1H), 1.31 (s, 12H).

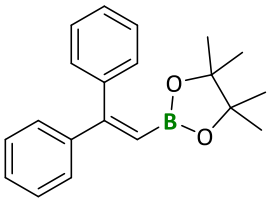
^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.47, 149.76, 148.79, 136.45, 123.08, 122.23, 83.48, 24.80.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.97.

These data are in agreement with those reported in the literature.[23]

HRMS (ESI) for **$C_{13}H_{19}BNO_2$ [M+H$^+$]$^+$:** calculated: 230.1467, found: 230.1472.

2-(2,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **14** (61% ,66 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.24 (m, 10H), 5.99 (s, 1H), 1.15 (s, 12H).

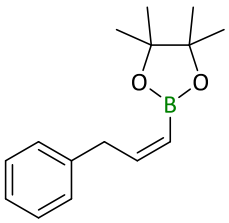
^{13}C NMR ($CDCl_3$, 100 MHz) δ 129.85, 128.29, 128.02, 127.99, 127.60, 127.54, 83.16, 24.62.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.66.

HRMS (ESI) for **$C_{20}H_{23}BO_2$ [M+H$^+$]$^+$:** calculated: 307.1869, found: 307.1877.

6.3.2. Spectral data for boron-Wittig *Z*-alkenyl pinacolboranes

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*Z*-1)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *Z*-**1** (36%, 23 mg) as a pale yellowish oil.

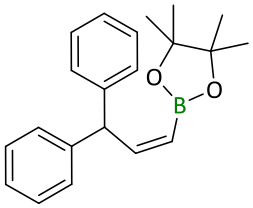
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.25 (m, 2H), 7.26 – 7.13 (m, 3H), 6.55 (dt, J = 14.3, 7.5 Hz, 1H), 5.43 (dt, J = 13.3, 1.4 Hz, 1H), 3.76 (dt, J = 7.6, 0.9 Hz, 2H), 1.30 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.69, 140.67, 128.64, 128.42, 125.92, 83.03, 38.67, 24.88.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.01.

HRMS (ESI) for **$C_{15}H_{21}BO_2$ [M+NH$_4^+$]$^+$:** calculated: 262.1979, found: 262.1978.

(*Z*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Z*-3)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *Z*-**3** (71%, 56 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 – 7.25 (m, 5H), 7.25 – 7.17 (m, 5H), 6.85 (dd, J = 13.2, 10.4 Hz, 1H), 5.65 (dd, J = 10.3, 06 Hz, 1H), 5.52 (dd, J = 13.2, 0.6 Hz, 1H), 1.28 (s, 12H).

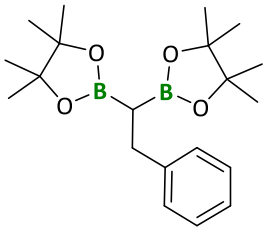
^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.14, 144.26, 128.42, 128.39, 126.15, 83.12, 51.99, 30.93, 24.90.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.09.

HRMS (ESI) for **$C_{21}H_{25}BO_2$ [M+NH_4^+]$^+$:** calculated: 338.2302, found: 338.2291.

6.3.3. Spectral data for 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

2,2'-(2-Phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (36)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **36** (30%, 160 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.21 (m, 4H), 7.14 (dd, J = 8.6, 5.9 Hz, 1H), 2.91 (d, J = 8.4 Hz, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 1.20 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.48, 128.35, 127.95, 125.33, 83.09, 65.86, 31.30, 24.78, 24.52.

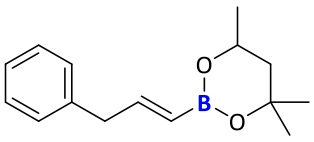
^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.70.

The characterization data are in agreement with those reported in the literature.[25]

HRMS (ESI) for **$C_{20}H_{32}B_2O_4$ [M+Na]$^+$:** calculated: 381.2392, found: 381.2392.

6.3.4. Spectral data for transborylation of alkenyl pinacolboranes

(*E*)-4,4,6-Trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (*E*-2)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *E*-**2** (89%, 64 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 – 7.17 (m, 2H), 7.11 (dt, J = 6.4, 1.2 Hz, 3H), 6.57 (dt, J = 17.6, 6.4 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.37 (d, J =

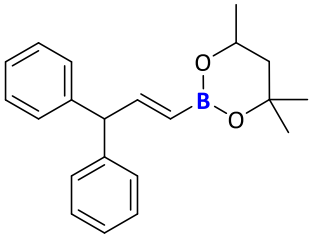
6.4 Hz, 2H), 1.69 (dd, J = 13.9, 3.0 Hz, 1H), 1.41 (dd, J = 13.9, 11.6 Hz, 1H), 1.20 (s, 6H), 1.17 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.01, 139.77, 128.96, 128.40, 126.01, 70.68, 64.65, 45.97, 42.07, 31.25, 28.12, 23.17.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.18.

HRMS (ESI) for **$C_{15}H_{21}BO_2$ [M+NH_4^+]$^+$:** calculated: 262.1978, found: 262.1998.

(*E*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*E*-4)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *E*-**4** (77%, 58 mg) as a pale yellowish oil.

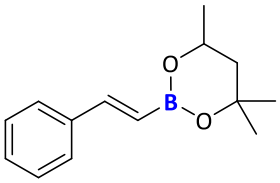
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 – 7.29 (m, 4H), 7.25 (m, 6H), 7.01 (dd, J = 17.6, 6.8 Hz, 1H), 5.37 (dd, J = 17.7, 1.5 Hz, 1H), 4.83 (dd, J = 6.9, 1.5 Hz, 1H), 4.26 (m, 1H), 1.82 (dd, J = 13.9, 2.9 Hz, 1H), 1.66 – 1.48 (m, 1H), 1.34 (d, J = 2.2 Hz, 6H), 1.20 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.43, 143.17, 132.43, 130.08, 128.86, 128.35, 128.30, 126.27, 70.71, 64.67, 56.62, 45.98, 31.25, 28.16.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 25.79.

HRMS (ESI) for **$C_{21}H_{25}BO_2$ [M+H^+]$^+$:** calculated: 320.7415, found: 320.7442.

(*E*)-4,4,6-Trimethyl-2-(2-phenylethenyl)-1,3,2-dioxaborinane (8)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **8** (62%, 45 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 – 7.43 (m, 2H), 7.33 – 7.20 (m, 4H), 6.09 (d, J = 18.2 Hz, 1H), 4.26 (m, 1H), 1.80 (dd, J = 13.9, 2.9 Hz, 1H), 1.54 (t, J = 12.7 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H).

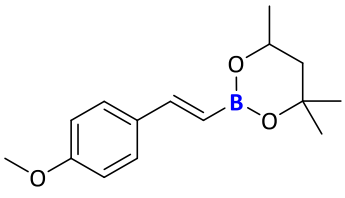
^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.49, 138.02, 128.45, 128.29, 126.97, 70.90, 64.85, 46.03, 31.29, 28.17, 23.21.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.24.

These data are in agreement with those reported in the literature.[26]

HRMS (ESI) for **$C_{14}H_{19}BO_2$ [M+H^+]$^+$:** calculated: 231.1556, found: 231.1569.

(*E*)-2-(4-Methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane (9)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **9** (80%, 62 mg) as a pale yellowish oil.

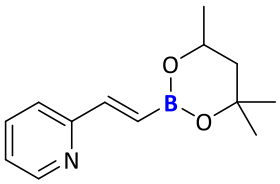
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.38 (m, 1H), 7.31 – 7.21 (m, 2H), 6.88 – 6.81 (m, 2H), 5.95 (d, J = 18.2 Hz, 1H), 4.27 (m, 1H), 3.81 (s, 3H), 1.82 (dd, J = 13.9, 2.9 Hz, 1H), 1.60 – 1.49 (m, 2H), 1.34 (s, 3H), 1.33 (s, 3H), 1.31 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.83, 146.04, 130.93, 128.29, 113.85, 70.83, 64.80, 55.28, 46.02, 31.31, 28.17, 23.24.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.25.

HRMS (ESI) for **$C_{15}H_{21}BO_3$ [M+H]$^+$:** calculated:261.1662, found:261.1658.

(*E*)-2-(2-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine (10)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **10** (56%, 45 mg) as a pale yellowish oil.

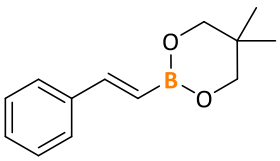
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.63 (td, J = 7.7, 1.9 Hz, 1H), 7.47 (dt, J = 8.0, 1.1 Hz, 1H), 7.39 (d, J = 18.2 Hz, 1H), 7.13 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 6.48 (d, J = 18.2 Hz, 1H), 4.28 (m, 1H), 1.82 (dd, J = 13.9, 3.0 Hz, 1H), 1.55 (dd, J = 13.9, 11.6 Hz, 1H), 1.33 (s, 6H), 1.30 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.35, 149.53, 146.37, 136.27, 122.55, 121.19, 70.97, 64.92, 45.99, 31.23, 28.14, 23.16.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.47.

HRMS (ESI) for **$C_{14}H_{19}BO_2$ [M+H$^+$]$^+$:** calculated: 230.1467, found: 230.1474.

(*E*)-5,5-Dimethyl-2-(2-phenylethenyl)-1,3,2-dioxaborinane (11)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **11** (68%, 26 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.46 (m, 2H), 7.38 – 7.23 (m, 5H), 6.11 (d, J = 18.3 Hz, 1H), 3.70 (s, 4H), 1.01 (s, 6H).

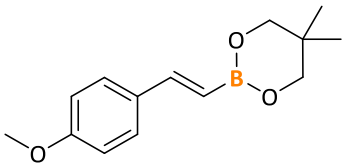
^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.13, 137.80, 128.52, 127.01, 72.22, 31.87, 21.89.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.48.

These data are in agreement with those reported in the literature.[23]

HRMS (ESI) for **$C_{13}H_{17}BO_2$ [2M+H$^+$]$^+$:** calculated: 432.2817, found: 432.2643.

(*E*)-2-(4-Methoxystyryl)-5,5-dimethyl-1,3,2-dioxaborinane (12)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **12** (64%, 53 mg) as a pale yellowish oil.

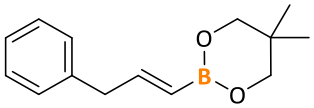
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 – 7.39 (m, 2H), 7.28 (d, J = 17.3 Hz, 1H), 6.92 – 6.80 (m, 2H), 5.95 (d, J = 18.2 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 4H), 0.98 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.01, 146.66, 130.69, 128.36, 113.92, 72.20, 55.30, 31.88, 24.83, 21.90.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 25.98.

HRMS (ESI) for **$C_{14}H_{19}BO_3$ [M+H]$^+$:** calculated: 247.1506, found: 247.1507.

(*E*)-5,5-Dimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (15)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **15** (48%, 33 mg) as a pale yellowish oil.

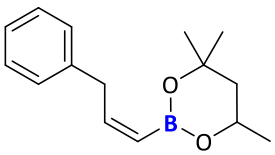
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.25 (m, 2H), 7.19 (t, J = 7.5 Hz, 3H), 6.67 (dt, J = 17.6, 6.4 Hz, 1H), 5.39 (dt, J = 17.6, 1.6 Hz, 1H), 3.62 (s, 4H), 3.46 (dd, J = 6.5, 1.6 Hz, 2H), 0.96 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.74, 139.59, 128.86, 128.42, 126.05, 72.08, 42.07, 31.77, 21.87.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 25.82.

HRMS (ESI) for **$C_{14}H_{19}BO_2$ [M+NH_4^+]$^+$:** calculated: 262.1978, found: 262.1978.

(*Z*)-4,4,6-Trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (*Z*-2)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **11** (69%, 59 mg) as a pale yellowish oil.

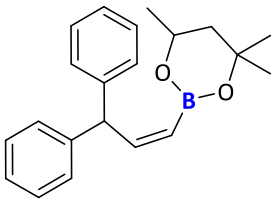
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.15 (m, 3H), 7.15 – 7.07 (m, 1H), 6.33 (dt, J = 13.5, 1.2 Hz, 1H), 5.25 (d, J = 13.5 Hz, 1H), 4.20 (m, 1H), 3.68 (d, J = 7.6, 2H), 1.74 (dd, J = 13.9, 2.9 Hz, 1H), 1.53 – 1.42 (m, 1H), 1.26 (d, 6H), 1.22 (d, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.70, 141.38, 128.67, 128.34, 125.73, 70.88, 64.78, 45.96, 37.98, 31.36, 28.25, 24.88, 23.25.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.23.

HRMS (ESI) for **$C_{15}H_{21}BO_2$ [M+NH_4^+]$^+$:** calculated: 262.1978, found: 262.1998.

(*S*,*Z*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*Z*-4)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded *Z*-**4** (32%, 20 mg) as a pale yellowish oil.

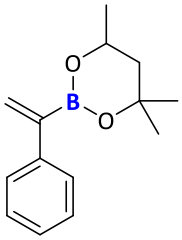
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 – 7.27 (m, 4H), 7.27 – 7.16 (m, 4H), 6.74 (dd, J = 13.4, 10.2 Hz, 1H), 5.76 (d, J = 10.2 Hz, 1H), 5.44 (d, J = 13.4 Hz, 1H), 4.27 (m, 1H), 1.81 (dd, J = 13.9, 2.9 Hz, 1H), 1.57 – 1.48 (m, 1H), 1.34 (d, J = 3.3 Hz, 3H), 1.31 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.24, 128.33, 125.98, 70.97, 64.82, 51.18, 45.85, 31.35, 30.94, 28.25, 23.23.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.29.

HRMS (ESI) for **$C_{21}H_{25}BO_2$ [M+NH_4^+]$^+$:** calculated: 338.23, found: 338.2291.

4,4,6-Trimethyl-2-(1-phenylvinyl)-1,3,2-dioxaborinane (17)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **17** (80%, 76 mg) as a pale yellowish oil.

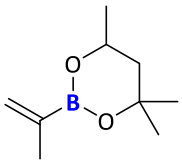
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.40 (m, 2H), 7.35 – 7.25 (m, 2H), 7.26 – 7.17 (m, 1H), 5.98 (d, J = 3.5 Hz, 1H), 5.90 (d, J = 3.5 Hz, 1H), 4.29 (m, 1H), 1.84 (dd, J = 13.9, 3.0 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.33 (s, 6H), 1.30 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.64, 128.79, 127.83, 127.58, 126.44, 71.19, 65.13, 45.91, 31.23, 28.13, 23.16.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.39.

HRMS (ESI) for **$C_{14}H_{19}BO_2$ [M+NH_4^+]$^+$:** calculated: 248.1822, found: 248.1831.

4,4,6-Trimethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborinane (19)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **19** (15%, 22 mg) as a pale yellowish oil.

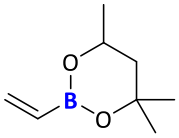
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.65 (m, 1H), 5.52 – 5.46 (m, 1H), 4.21 (m, 1H), 1.77 (d, J = 17.1 Hz, 1H), 1.70 (s, 3H), 1.53 – 1.42 (m, 1H), 1.29 (s, 6H), 1.26 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 126.70, 70.60, 64.67, 45.89, 31.26, 28.13, 24.79, 23.18, 20.92.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.01.

HRMS (ESI) for **$C_9H_{17}BO_2$ [M]$^+$:** calculated: waiting for result.

4,4,6-Trimethyl-2-vinyl-1,3,2-dioxaborinane (21)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **21** (30%, 31 mg) as a pale yellowish oil.

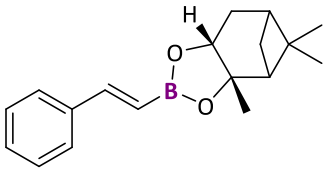
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (dd, J = 18.7, 5.1 Hz, 1H), 5.86 (dd, J = 13.4, 5.0 Hz, 1H), 5.77 (dd, J = 18.8, 13.4 Hz, 1H), 4.22 (m, 1H), 1.79 (dd, J = 13.9, 3.0 Hz, 1H), 1.58 – 1.49 (m, 1H), 1.30 (s, 6H), 1.27 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.76, 70.76, 64.71, 45.96, 31.21, 28.10, 23.13.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 25.84.

HRMS (ESI) for **$C_8H_{15}BO_2$ [M]$^+$:** calculated: waiting for result.

(3a*R*,4*S*,6*S*,7a*R*)-3a,5,5-Trimethyl-2-((*E*)-styryl)hexahydro-4,6-methanobenzo[*d*][1,3,2] dioxaborole (23)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **23** (88%, 94 mg) as a pale yellowish oil.

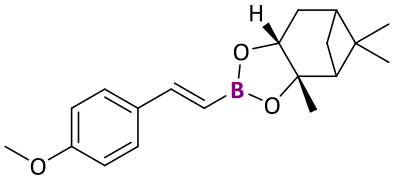
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 – 7.46 (m, 2H), 7.41 (d, J = 18.5 Hz, 1H), 7.39 – 7.25 (m, 3H), 6.20 (d, J = 18.4 Hz, 1H), 4.38 (dd, J = 8.7, 1.9 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.30 – 2.19 (m, 1H), 2.12 (t, J = 6.0, 4.8 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.46 (s, 3H), 1.31 (s, 3H), 1.21 (d, J = 10.9 Hz, 1H), 0.88 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.61, 137.65, 129.02, 128.71, 128.10, 127.19, 85.96, 78.00, 51.55, 39.68, 38.33, 35.68, 28.81, 27.25, 26.60, 24.18.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.25.

HRMS (ESI) for **$C_{18}H_{23}BO_2$ [2M]$^+$:** calculated: 564.3582, found: 564.3583.

(3a*S*,4*S*,6*S*,7a*R*)-2-((*E*)-4-Methoxystyryl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (24)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **24** (72%, 86 mg) as a pale yellowish oil.

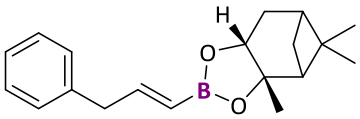
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.40 (m, 2H), 7.36 (d, J = 18.4 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.03 (d, J = 18.4 Hz, 1H), 4.36 (dd, J = 8.7, 1.9 Hz, 1H), 3.82 (s,

3H), 2.39 (m, 1H), 2.30 – 2.17 (m, 1H), 2.11 (dd, J = 6.1, 4.9 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.45 (s, 3H), 1.31 (s, 3H), 1.26 – 1.16 (m, 2H), 0.87 (s, 3H), 0.85 (d, J = 8.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.29, 149.01, 130.47, 130.30, 128.46, 113.98, 85.70, 77.80, 65.86, 55.30, 51.45, 39.57, 38.20, 35.59, 28.69, 27.12, 26.47, 24.04, 15.29.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.88.

(3a*S*,4*S*,6*S*,7a*R*)-3a,5,5-Trimethyl-2-((*E*)-3-phenylprop-1-en-1-yl)hexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (25)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **25** (80%, 70 mg) as a pale yellowish oil.

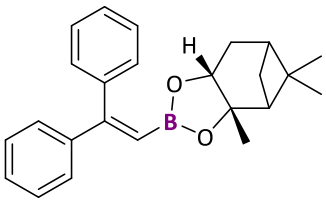
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.31 (m, 2H), 7.31 – 7.22 (m, 3H), 6.84 (dt, J = 17.8, 6.4 Hz, 1H), 5.55 (dt, J = 17.8, 1.6 Hz, 1H), 4.36 (dd, J = 8.7, 1.9 Hz, 1H), 3.56 (m, 2H), 2.41 (ddt, J = 14.0, 8.7, 2.2 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.12 (dd, J = 6.1, 4.9 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.46 (s, 3H), 1.36 (s, 3H), 1.22 (d, J = 10.9 Hz, 1H), 0.98 – 0.91 (m, 1H), 0.92 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.33, 139.14, 128.91, 128.45, 126.16, 85.59, 77.70, 51.37, 42.31, 39.52, 38.15, 35.48, 28.64, 27.10, 26.44, 24.01.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.57.

HRMS (ESI) for **$C_{19}H_{25}BO_2$ [M+NH_4^+]$^+$:** calculated: 314.2291, found: 314.2302.

(3a*S*,4*S*,6*S*,7a*R*)-2-(2,2-Diphenylvinyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (26)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **26** (78%, 73 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.20 (m, 10H), 6.01 (s, 1H), 4.15 (dd, J = 8.7, 2.0 Hz, 1H), 2.24 – 2.09 (m, 2H), 1.95 (t, J = 5.5 Hz, 1H), 1.83 (tt, J = 5.9, 3.1 Hz, 1H), 1.63 (ddd, J = 14.5, 3.4, 2.1 Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H), 1.10 (d, J = 10.7 Hz, 1H), 0.77 (s, 3H).

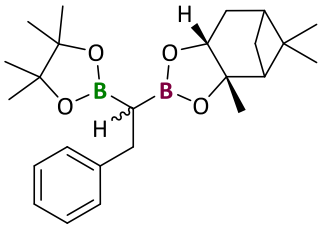
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.96, 143.09, 141.92, 132.42, 129.83, 128.08, 128.03, 127.96, 127.63, 127.57, 85.44, 77.73, 65.87, 51.25, 39.47, 38.13, 35.22, 28.44, 27.08, 26.51, 24.00, 15.30.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.89.

HRMS (ESI) for **$C_{24}H_{27}BO_2$ [M+H^+]$^+$:** calculated: 359.2191, found: 259.2182.

6.3.5. Spectral data for *gem*-diboryl alkanes

(3a*S*,4*S*,6*S*)-3a,5,5-Trimethyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)hexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (37)



Purified by flash column chromatography (hexane:diethyl ether = 100:1) yielded **37** (39%, 20 mg) as a pale yellowish oil.

Compound **37** was isolated as a mixture of 1:1 of diastereoisomers.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.10 (m, 8H), 7.05 (m, 2H), 4.15 (dd, J = 8.8, 1.9 Hz, 1H), 4.13 (dd, J = 8.8, 1.9 Hz, 1H), 2.83 (dd, J = 8.4, 5.2 Hz, 2H), 2.81 (dd, J = 8.4, 5.2 Hz, 2H), 2.04 (m, 2H), 1.95 (q, J = 5.4 Hz, 1H), 1.95 (m, 2H), 1.82 – 1.66 (m, 4H), 1.24 (s, 3H), 1.23 (s, 3H), 1.19 (s, 3H), 1.18 (s, 3H), 1.12 (s, 12H), 1.10 (s, 12H), 0.99 (d, J = 10.9 Hz, 2H), 0.98 (d, J = 10.9 Hz, 2H), 0.74 (s, 3H), 0.73 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.47, 144.42, 128.38, 128.30, 128.00, 127.98, 125.36, 85.54, 83.12, 77.75, 77.74, 51.27, 39.51, 39.46, 38.09, 38.07, 35.56, 35.53, 31.49, 31.43, 29.71, 28.64, 28.58, 27.10, 26.40, 24.82, 24.79, 24.54, 23.99.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.73.

HRMS (ESI) for **$C_{24}H_{36}B_2O_4$ [M+NH_4^+]$^+$:** calculated: 428.3143, found: 428.315.

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