Contributions to Precise Skeletal Editing via Alkenylboranes

Paula Dominguez Molano

UNIVERSITAT ROVIRA i VIRGILI

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DOCTORAL THESIS
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PhD Thesis

Supervised by Prof. María Elena Fernández Gutiérrez

Departament de Química Física i Inorgànica

UNIVERSITAT ROVIRA i VIRGILI

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DEPARTAMENT DE QUÍMICA
FÍSICA i INORGÀNICA
Universitat Rovira i Virgili

Prof. María Elena Fernández Gutiérrez, professora catedràtica del Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili,

FAIG CONSTAR que aquest treball, titulat:

"**Contributions to Precise Skeletal Editing via Alkenylboranes**"

que presenta Paula Dominguez Molano per a l'obtenció del títol de Doctor, i que acompleix els requeriments per a poder optar a Menció Internacional, ha estat realitzat sota la meva direcció al Departament de Química Física i Inorgànica de la Universitat Rovira i Virgili.

Tarragona, 1 de setembre de 2024

Prof. María Elena Fernández Gutiérrez

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Agraïments

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Contents

Abbreviations and acronyms list

δ	Chemical shift
Å	Angstrom
Ac	acyl
acac	Acetylacetonate
AcOEt	Ethyl acetate
Ad	Adamantyl
Ar	Aryl
aq.	Aqueous
b	Broad
9-BBN	9-Borabicyclo[3.3.1]nonane
bdpp	2,4-Bis(diphenylphosphino)pentane
BenzP*	1,2-Bis(t-butylmethylphosphino)benzene
Bhex	Hexylene glycolato boryl
BINAP	(2,2'-bis(diphenylphosphino)-1,1'- binaphthyl)
Bn	Benzyl
BoPhoz	(2R,5R)-1-(2-((2R,5R)-2,5-dimethylphospholan-1-yl)phenyl)-2,5-dimethylphospholane 1-oxide
Bpin	Pinacolato boryl
bpy	2,2'-bipyridine
BQ	1,4-Benzoquinone
Bu	butyl
°C	Degree Celsius
cat	catechol
Cy	cyclohexyl
COD	1,5-Cyclooctadiene
coe	Cyclooctene
CPME	Cyclopentyl methyl ether
d	Doublet
dan	1,8-Diaminonaphthalene
dba	Dibenzylideneacetone

DCE	1,2-dichloroethane
DCM	Dichloromethane
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
DIOP	(2,3-O-isopropylidene-2,3-dihydroxy-1,4- bis(diphenylphosphino)butane)
DPPB	1,4-(bis(diphenylphosphino)butane
dppbz	1,2-Bis(diphenylphosphino)benzene
dr	Diastereomeric ratio
DtBPF	1,1'-bis(di-*tert*-butylphosphanyl)ferrocene
dtbpy	4,4'-di-tert-butyl-2,2'-bipyridine
DuPhos	2-Dicyclohexylphosphino-2′,6′ - diisopropoxybiphenyl
E	electrophile
ee	enantiomeric excess
EDG	Electron donating group
equiv	Equivalents
er	enantiomeric ratio
Et	Ethyl
Et_2O	Diethyl ether
EtDuPhos	1,2-Bis((2*R*,5*R*)-2,5-diethylphospholano)benzene
EWG	Electron withdrawing group
FG	functional group
GC-MS	Gas chromatography mass spectroscopy
h	hours
hex	Hexyl
HRMS	High resolution mass spectrometry
Hz	Hertz
IMes	1,3-Bis(2,4,6-trimethylphenyl)-1,3- dihydro-2H-imidazol-2-ylidene
[IPA-Co]	Iminopyridineamine-cobalt catalyst
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2- ylidene
J	Coupling constant
JessePhos	*tert*-butylbis(3,5-di-*tert*-butylphenyl)phosphane

JohnPhos	(2-Biphenyl)di-*tert*-butylphosphine
L	Ligand
LG	Leaving group
LiTMP	Lithium 2,2,6,6-tetramethylpiperidide
m	Multiplet
MeCN	Acetonitrile
MeOH	Methanol
MIDA	*N*-methyliminodiacetic acid
Mp	Melting point
MS	Molecular sieves
m/z	Mass charge relation
MTBE	Methyl *tert*-butyl ether
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
N-Dpp	*N*-diphenylphosphinyl
neo	neopentyl glycolato
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
NOE	Nuclear Overhauser effect
Nu	Nucleoplile
p	Pentet
pai	Pinanediolato
Ph	Phenyl
PG	Protecting group
pin	Pinacol
Piv	Pivalic acid
$PhCF_3$	Trifluorotoluene
ppm	Parts per million
PSiP	Pincer-like bis(phosphino)silyl ligand
q	Quartet
QuinoxP*	2,3-Bis(tertbutylmethylphosphino) quinoxaline

RL	Large group
RS	Small group
rt	Room temperature
r.t.	Room temperature
RuPhos	2-Dicyclohexylphosphino-2′,6′- diisopropoxybiphenyl
s	Singlet
SE	Electrophilic substitution
SN	Nucleophilic substitution
SEGPhos	5,5′-Bis(diphenylphosphino)-4,4′-bi- 1,3-benzodioxole
SIMes	1,3-Bis(2,4,6-trimethylphenyl)-4,5- dihydroimidazol-2-ylidene
SPhos	2-Dicyclohexylphosphino-2′,6′- dimethoxybiphenyl
(*S*,*S*)-bdpp	(2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane
t	Triplet
T	Temperature
TBDMS	*tert*-butyldimethyllsilyl
THF	Tetrahydrofuran
TMS	Trimethylsilyl
TMSDM	(trimethylsilyl)diazomethane
Ts	Tosyl group (*p*-toluenesulfonyl)
TS	Transition state
Xantphos	4,5-Bis(diphenylphosphino)-9,9- dimethylxanthine

CHAPTER I

General introduction

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1.1. Organoboron compounds

Over the past 70 years, organoboron compounds have significantly transformed organic chemistry, offering several essential synthetic applications. Remarkable discoveries and immense potential of this field ensure that the synthesis and reactivity of organoboron compounds remain at the cutting edge of scientific research.

The chemical properties of the boron atom resemble those of carbon and silicon more closely than those of other group 13 elements although boron is more electron deficient due to the empty *p*-orbital.[1] Organoboron compounds are generally trivalent neutral compounds. Consequently, the boron atom is sp^2 hybridised, exhibiting trigonal planar geometry, with an empty *p*-orbital that justifies its Lewis acidic properties. This Lewis acidity of trivalent boron compounds has been extensively exploited in a variety of versatile reactions.

Organoboron compounds, characterised by at least one carbon-to-boron bond, could be classified into various categories such as boranes, borohydrides, boronic acids, boronic esters, boronamides, trifluoroborates, among others (Figure 1.1a).[2] Boron could also form negatively charged tetravalent compounds, which adopt a tetrahedral geometry, and are known as boron'ate' compounds. In addition, these organoboron compounds could exhibit different reactivity by adjusting the substitutions around the boryl moiety (Figure 1.1b).

In addition, the chemistry of diboron compounds has been extensively explored over the past two decades (Figure 1.1c). This exploration has revealed many intriguing structural features and reaction patterns. More importantly, diboron compounds have become central to both metal-catalysed and metal-free methodologies for forming B–C bonds and other processes. The most relevant diboron compounds for this thesis are shown in Figure 1.1c.

On the other hand, *geminal* diborylalkanes are considered versatile building blocks for synthesising a variety of structurally complex organic compounds. Compared to other 1,1-organodimetallic reagents, *gem*-diborylalkane derivatives highlight their stability, ready accessibility, functional group tolerance, and low toxicity (Figure 1.1d).

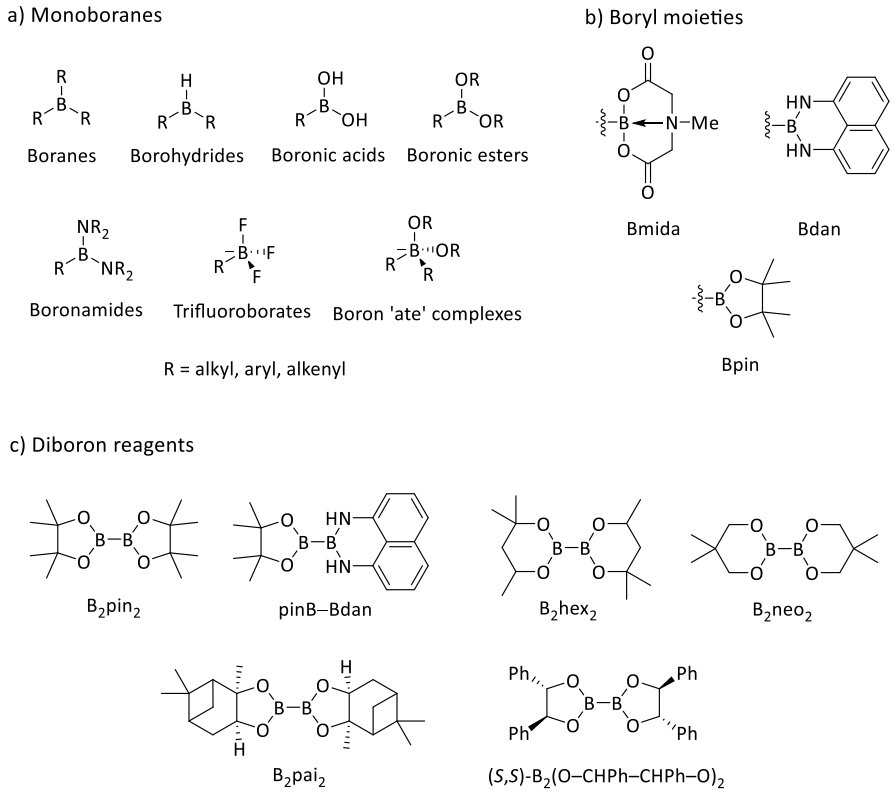


Figure 1.1. Selected examples of a) monoboranes, b) boryl moieties, c) diboron reagents, and d) *gem*-diborylalkanes.

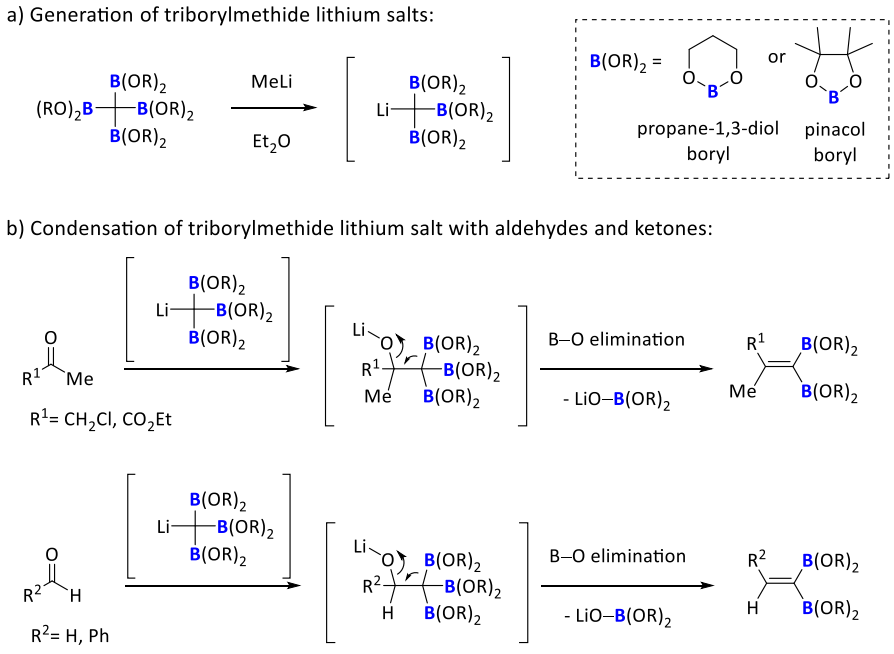
1.2. *Gem*-diborylalkenes: synthesis of valuable building blocks

Given the growing significance of *gem*-diboron compounds, 1,1-diborylalkenes constituted a novel subclass with promising potential for synthesising multisubstituted olefins with stereocontrol through sequential reactions at the two C–B bonds. In this context, *gem*-diboron compounds were bifunctional species containing two boryl moieties in a *geminal* position.

Several routes for the synthesis of *gem*-diborylalkenes have been developed, based on the specific C–B bond formation strategy. This section details the most significant synthetic methods to prepare both symmetrical and unsymmetrical *gem*-diborylalkenes.

1.2.1. Condensation of polyborated compounds with aldehydes or ketones followed by B–O elimination

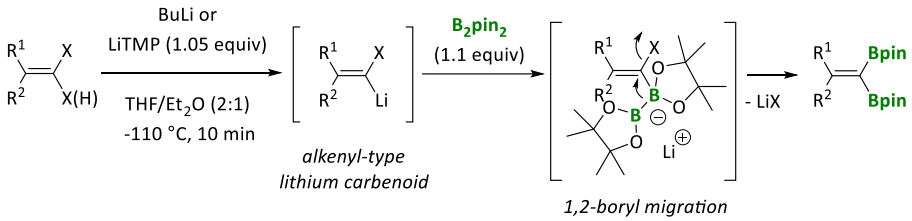
In 1974, Matteson and co-workers described the generation of triborylmethide lithium salts, from tretraborylmethane in the presence of methyllithium, and its reactivity with aldehydes and ketones leading the formation of *gem*-diborylalkenes *via* B–O elimination (Scheme 1.1).[3] The reactivity was investigated using both propane-1,3-diol and pinacol boryl moieties. Functional groups such as α-chloroalkyls and esters were well-tolerated when ketones were used as coupling partners. Additionally, benzaldehyde and formaldehyde underwent condensation, yielding trisubstituted *gem*-diborylalkenes.



Scheme 1.1. Synthesis of *gem*-diborylalkenes by condensation of polyborated compounds with carbonyl groups.

1.2.2. *Geminal* diboration of 1,1-dihaloalkenes or 1-haloalkenes

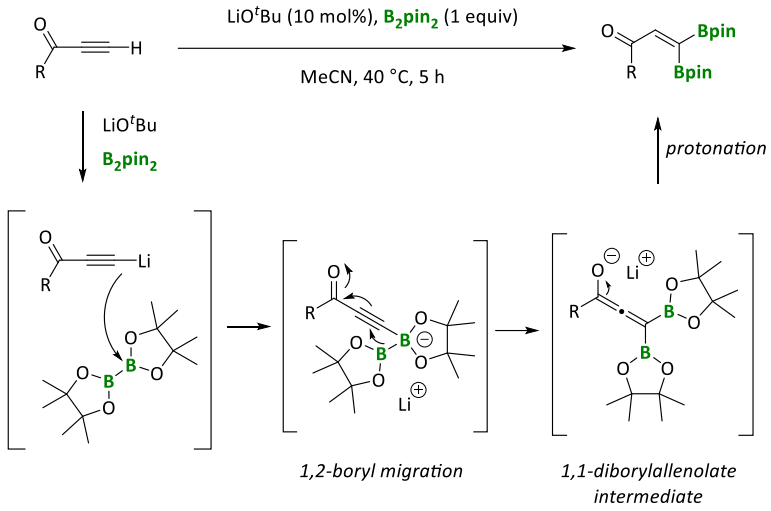
In 2001, Hiyama, Shimizu, and co-workers discovered that alkylidene-type lithium carbenoids could react with bis(pinacolato)diboron, allowing the conversion of 1,1-dihaloalkenes or 1-haloalkenes into 1,1-diborylalkenes (Scheme 1.2).[4a] The reaction took place in the presence of BuLi or LiTMP, with 1,1-dihaloalkenes forming alkylidene-type lithium carbenoid intermediates. The subsequent addition of B_2pin_2 allowed the formation of the corresponding *gem*-diborylalkenes by 1,2-migration of the boryl group in the intermediate alkenyl–B–B species. Additionally, the same research group reported the *gem*-diborylation of 1-haloalkenes using a similar strategy involving lithium carbenoid species (Scheme 1.2).[4b]



Scheme 1.2. *Geminal* diboration of alkylidene-type carbenoids with B_2pin_2.

1.2.3. *Geminal* diboration of terminal alkynes

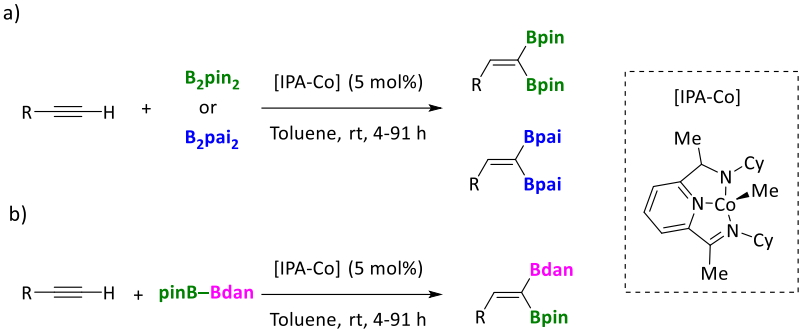
In 2015, Ohmiya, Sawamura and co-workers reported the 1,1-diboration of terminal alkynes with B_2pin_2 using acetylenic esters, amides, and imidazole-type compounds as substrates (Scheme 1.3).[5] The authors proposed a mechanism initiated by the deprotonation of the activated terminal alkyne with LiO^tBu, leading to the formation of a lithium acetylide. This intermediate could then react with B_2pin_2 to form an alkynylborate intermediate. The terminal boryl group of the intermediate adduct could migrate to the *sp*-hybridised carbon atom of the alkyne moiety, followed by the formation of 1,1-diborylallenolate. This sequence was completed by protonation to the final *gem*-diborated alkene product. LiO^tBu would be regenerated, thus making the overall process catalytic in this reagent.



Scheme 1.3. Transition-metal-free diboration of terminal alkynes in the presence of catalytic LiO^{t}Bu.

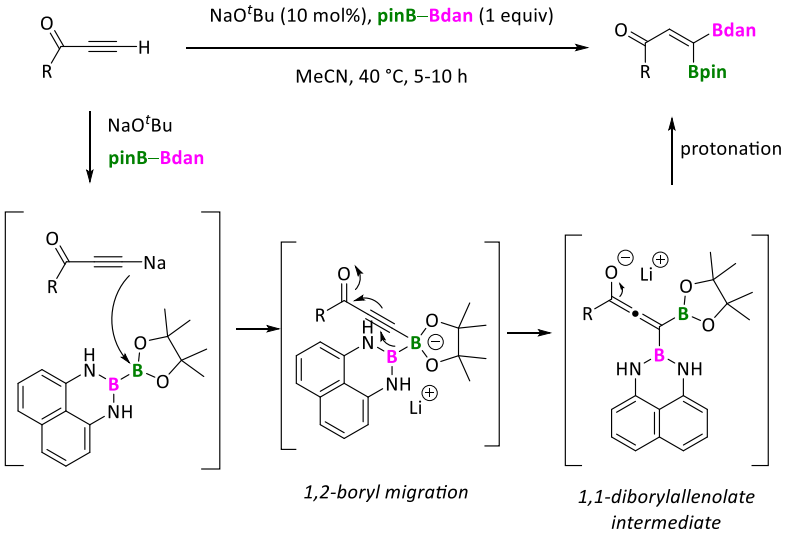
Alternatively, Chirik and co-workers developed a cobalt-catalysed diboration of terminal alkynes by an iminopyridineamine-cobalt complex ([IPA-Co]) and B_2pin_2.[6] The reaction proceeded efficiently at room temperature with excellent 1,1-selectivity and broad functional group tolerance, including *tert*-butyldimethylsilyl ether (TBDMS), acetal, ester, phthalimide, nitrile, and secondary amide, as well as a terminal double bond, which remains unreactive under the reaction conditions (Scheme 1.4). The reaction could also be performed with bis[(+)-pinanediolato]diboron, yielding the corresponding symmetrical *gem*-diborylalkenes.

On the other hand, when the non-symmetrical diboron reagent Bpin–Bdan (dan = 1,8-diaminonaphthalene) was used, the 1,1-diboration of terminal alkynes resulted in the stereoselective formation of trisubstituted olefins with well-defined stereochemistry (Scheme 1.4). The Bdan moiety was placed selectively *trans* to the alkyl substituents of the alkenes. This reaction required a temperature of 50 °C, likely due to the more challenging activation of the pinB–Bdan reagent by the cobalt catalyst.



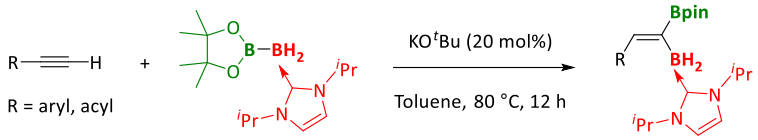
Scheme 1.4. Co-catalysed 1,1-diboration of terminal alkynes with a) B_2pin_2 or (+)-B_2pai_2 and b) pinB–Bdan.

In 2020, Marder and co-workers reported the stereoselective 1,1-diboration of terminal alkynes with Bpin–Bdan catalysed by NaO^{t}Bu affording unsymmetrical 1,1-diborylacrylates and 1,1-diborylacrylamides containing two different boryl groups in a regio- and stereoselective fashion (Scheme 1.5).[7] The reaction proceeded by 1,2-migration of the Bdan moiety generating an allenolate species.



Scheme 1.5. Transition metal-free diboration reaction to prepare unsymmetrical 1,1-diborylalkenes.

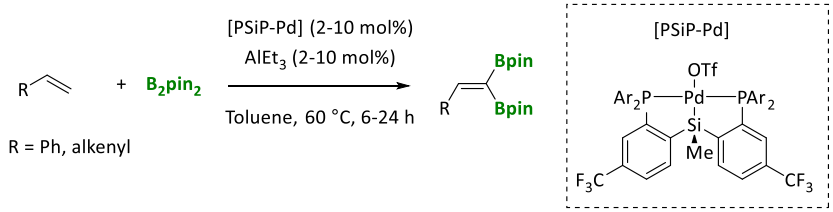
More recently, Lyu and co-workers studied the stereoselective unsymmetrical 1,1-diborylation reaction of alkynes using a neutral sp^2–sp^3 diboron reagent (NHC)BH_2–Bpin (Scheme 1.6).[8] This method offered a one-step synthesis from readily available substrates and enables the synthesis of (*E*)-selective unsymmetrical diborylalkenes with the sp^3 boryl being *cis* to the β-substituents on the olefin.



Scheme 1.6. Stereoselective unsymmetrical 1,1-diborylation reaction of alkynes using (NHC)BH_2–Bpin.

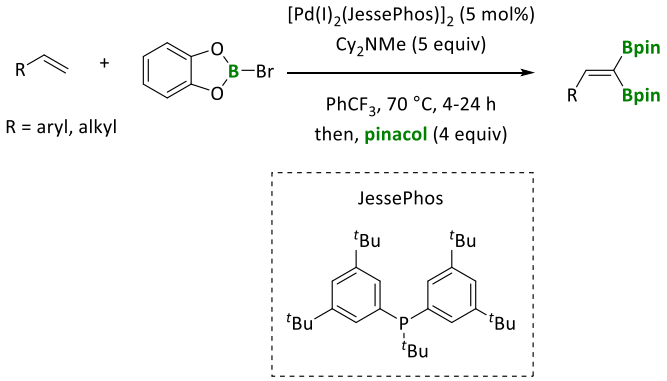
1.2.4. Dehydrogenative borylation of alkenes

Iwasawa and co-workers devised an efficient method for preparing 1,1-diborylalkenes from simple alkenes and diboron reagents through a palladium-catalysed double dehydrogenative borylation reaction (Scheme 1.7).[9,10] This process involved a monoborylpalladium(II) complex containing a PSiP-pincer-type ligand as the key catalytic species together with $AlEt_3$. Using terminal alkenes with electronically activated bulky groups and 2 equivalents of bis(pinacolato)diboron resulted in the formation of *gem*-diborylalkenes.



Scheme 1.7. Pd-catalysed double dehydrogenative borylation of alkenes.

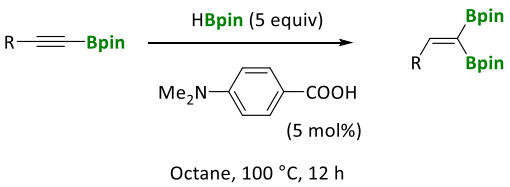
Additionally, Watson and co-workers reported palladium-catalysed boron-Heck reaction of terminal alkenes to afford symmetrical *gem*-diborylalkenes (Scheme 1.8).[11] The reaction accommodated aliphatic alkenes bearing a variety of functional groups, including halides, alkylsilanes, ethers, and silyl ethers. Likewise, aromatic alkenes with electron-donating or electron-withdrawing groups underwent a boron-Heck reaction to produce the corresponding *gem*-diborylalkenes. Treatment of the reaction mixture with 4 equivalents of pinacol was required to exchange the two cathecolboronic esters with the two pinacolboronic ester groups in the resulting *gem*-diborylalkenes.



Scheme 1.8. Pd-catalysed boron-Heck reaction of terminal alkenes.

1.2.5. Hydroboration of alkynylboranes

Jin and co-workers showed that alkynylboranes underwent hydroboration with HBpin in the presence of a catalytic amount of carboxylic acid, yielding the corresponding *gem*-diborylalkenes with exclusive regioselectivity (Scheme 1.9).[12] However, other hydroborating reagents, such as 9-BBN or HBcat, resulted incompatible with this organocatalytic reaction.

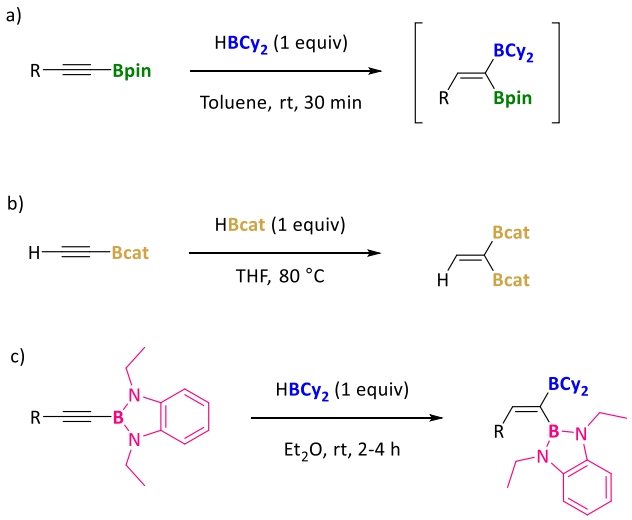


Scheme 1.9. Carboxylic acid-catalysed hydroboration of alkynylboranes with HBpin.

Alternative hydroborating reagents could be used for the non-catalysed hydroboration of alkynylboranes. For instance, $HBCy_2$ allowed straightforward addition to terminal alkynylboranes, even at room temperature, in a stereoselective manner (Scheme 1.10a).[13,14]

In this context, Siebert and co-workers achieved the non-catalysed hydroboration of ethynyl(catechol)boronic ester with one equivalent of catecholborane (HBcat), producing the corresponding 1,1-di(catecholboryl)ethene (Scheme 1.10b).[15] The reaction required a higher temperature (80 °C) to afford a quantitative yield of the corresponding product.

Additionally, Neumann and co-workers investigated the hydroboration of alkynylboranes containing 1,3,2-benzodiazaborole moieties with one equivalent of dicyclohexylborane ($HBCy_2$), resulting in the regioselective formation of unsymmetrical *gem*-diborylalkenes as the major regioisomer (Scheme 1.10c).[16]



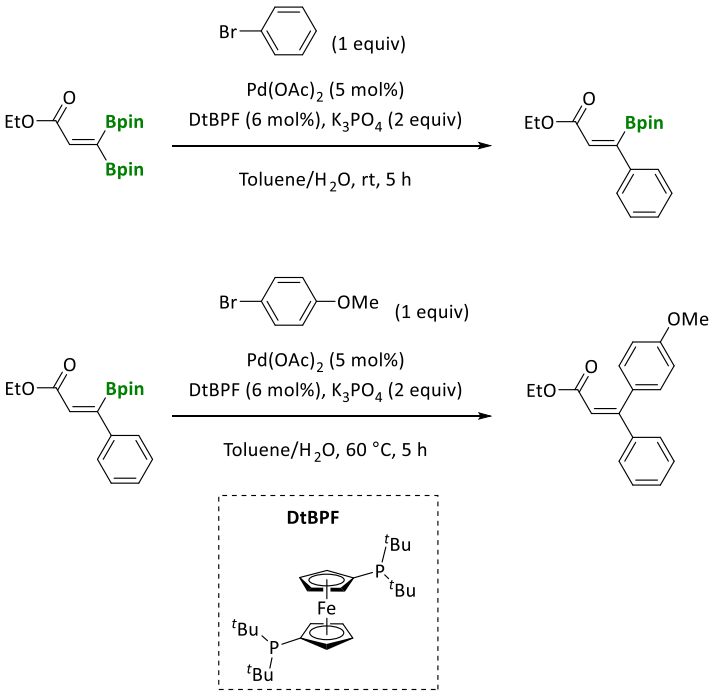
Scheme 1.10. Hydroboration of alkynylboranes through non-catalysed reaction.

1.3. Reactivity of *gem*-diborylalkenes

The presence of two *geminal* boryl moieties, in an alkene substrates, enhanced the versatility of the compound, since each boryl group could be differentiated and transformed stepwise enabling the synthesis of multisubstituted alkenes. Under optimised reaction conditions, *geminal* boryl groups could be selectively differentiated. Additionally, the substituents on the alkene could determine the selective boryl activation. This section describes the most interesting stepwise functionalisation of symmetrical and unsymmetrical *gem*-diborylalkenes.

1.3.1. Symmetrical *gem*-diborylalkenes

Ohmiya, Sawamura, and co-workers reported a sequential Suzuki-Miyaura coupling reaction of symmetrical 1,1-diborylacrylates with aryl bromides, in the presence of palladium acetate with DtBPF (DtBPF = 1,1'-bis(di-*tert*-butylphosphanyl)ferrocene) (Scheme 1.11).[5] The cross-coupling reaction proceeded selectively at the boron site *trans* to the ester group, probably due to the steric nature of the ester group. A second cross-coupling with 4-bromoanisole was conducted to yield an isomerically pure trisubstituted alkene with a *Z*/*E* ratio greater than 99:1. Notably, the first cross-coupling reaction occurred at room temperature while the second one required heating to 60 °C.

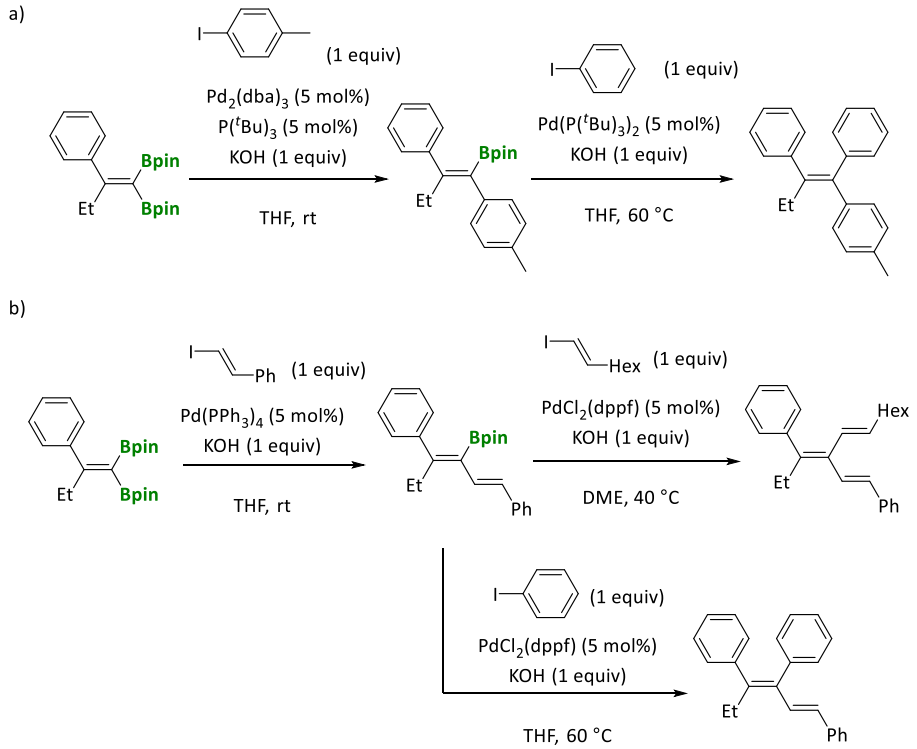


Scheme 1.11. Pd-catalysed sequential Suzuki-Miyaura coupling reaction.

1,1-Diborylalkenes could undergo stereoselective cross-coupling with aryl iodides to produce (*E*)-alkenylboronates as single isomers and successive couplings provided a fully stereocontrolled route to triarylated alkenes.[17] Using this concept, Hiyama and co-workers described a sequential cross-coupling of 1,1-diborylalkenes to prepare

tetrasubstituted alkenes (Scheme 1.12a).[18] The initial cross-coupling occurred at room temperature through Suzuki-Miyaura cross-coupling at the boryl moiety placed *trans* to the bulkier group, while the second one required 60 °C, suggesting a higher energy barrier.

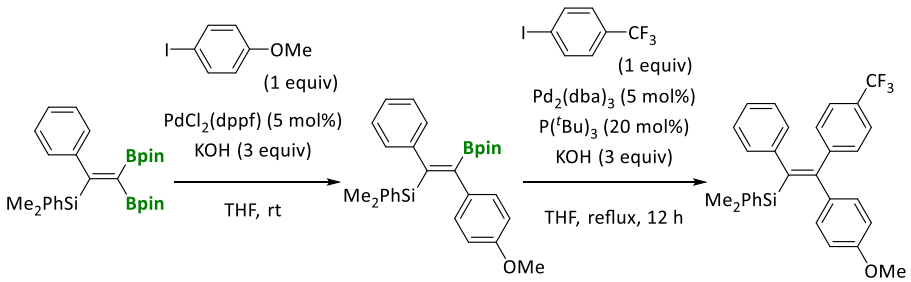
The same researchers extended this stereocontrolled coupling between 1,1-diborylalkenes and alkenyl iodides or bromides, yielding 3-borylated 1,3-dienes with good yields and high (*E*) selectivity (Scheme 1.12b).[18] Subsequent Pd-catalysed couplings with alkenyl or aryl iodides allowed the stereocontrolled formation of [3]dendralene or triphenylated 1,3-dienes.



Scheme 1.12. Stereoselective cross-coupling to afford triarylated alkenes and triarylated 1,3-dienes.

Nishihara and co-workers have developed a method for the highly chemoselective arylation of 1-phenyl-1-silyl-2,2-diborylethenes via Suzuki-Miyaura coupling, yielding (*Z*)-1-silyl-2-borylstilbene derivatives.[19] They identified $PdCl_2$(dppf) as an effective catalytic system for this selective arylation at room temperature, producing the (*Z*)-

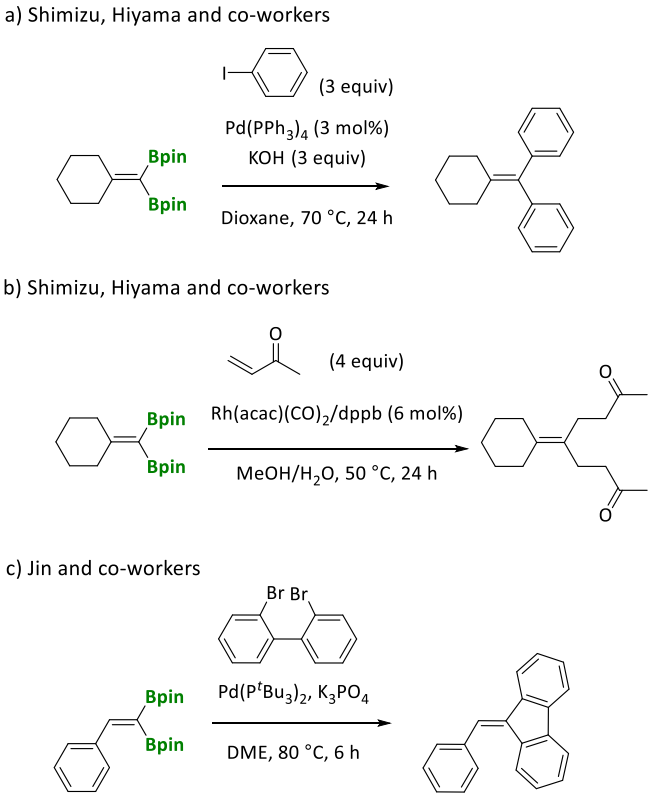
stereoisomer as the major triarylated product (Scheme 1.13). The C–C bond formation occurred predominantly at the position *cis* to the $SiMe_2Ph$ group, demonstrating significant discrimination between the *geminal* boryl groups. Subsequent cross-coupling reaction with the remaining boryl moiety provided access to triarylated compounds.



Scheme 1.13. Chemoselective arylation of 1-phenyl-1-silyl-2,2-diborylethenes.

A complementary method for the double cross-coupling of 1,1-diborylalkenes was developed, aimed at converting both C–B bonds into symmetric C–C bonds. Shimizu, Hiyama, and co-workers devised a convenient $Pd(PPh_3)_4$-catalysed double arylation of 1,1-diborylmethylenecyclohexane with iodobenzene at 70 °C (Scheme 1.14a).[4] Alternatively, the same group studied the Rh-catalysed Michael-type double addition of 1,1-diborylmethylenecyclohexane to methyl vinyl ketone that proceeded smoothly, yielding the corresponding 1,7-diketone in high yield (Scheme 1.14b).[4]

Similarly, Jin and co-workers showcased the synthetic utility of 1,1-diborylalkenes through double annulative Suzuki–Miyaura coupling with 2,2'-dibromo-1,1'-biphenyl in the presence of $Pd(PPh_3)_4$ catalyst, yielding 9-benzylidene-9H-fluorene in high yield (Scheme 1.14c).[12]

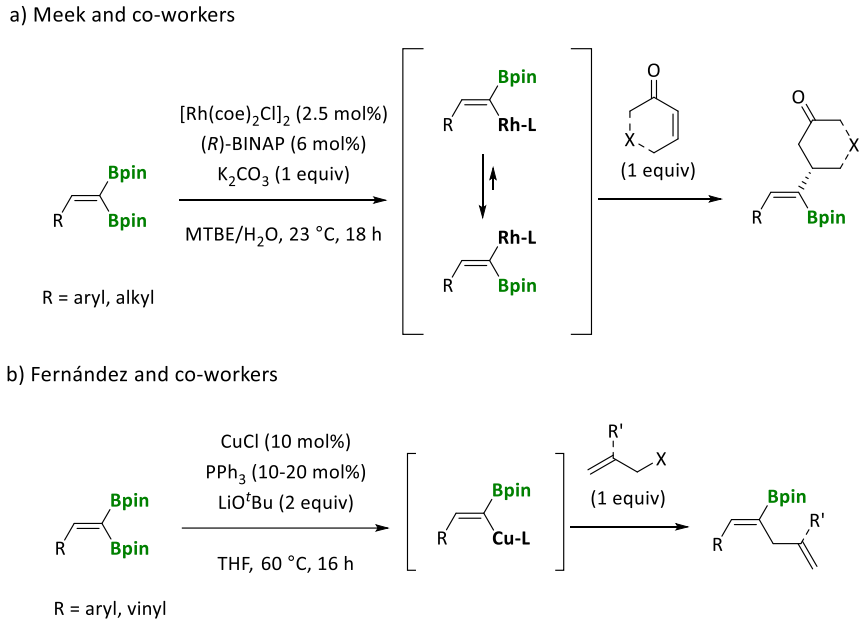


Scheme 1.14. Pd-catalysed double cross-coupling of 1,1-diborylalkenes.

Rhodium complexes have been shown to non-selectively activate both C–Bpin fragments on substituted 1,1-diborylalkenes.[4] However, in 2019, Meek and co-workers reported a rhodium-catalysed conjugate addition method to synthesise 1,4-keto-alkenylboronate ester compounds in an enantioselective fashion (Scheme 1.15a).[20] The stereoselectivity was justified on the basis of the fact that the (*Z*)-α-borylalkenyl Rh complex tended to isomerise into the (*E*)-α-borylalkenyl Rh complex, which underwent faster 1,4-addition to cyclic enones, generating almost exclusively the (*E*)-trisubstituted alkene.

More recently, Fernández and co-workers investigated a copper-catalysed chemoselective activation of 1,1-diborylalkenes, enabling selective coupling reactions that resulted in the formation of (*Z*)-skipped dienes (Scheme 1.15b).[21] In this context, the energetically preferred formation of (*Z*)-α-borylalkenyl copper (I) species, followed

by a subsequent nucleophilic attack, explained the stereoselective nucleophilic substitution with allyl bromides.

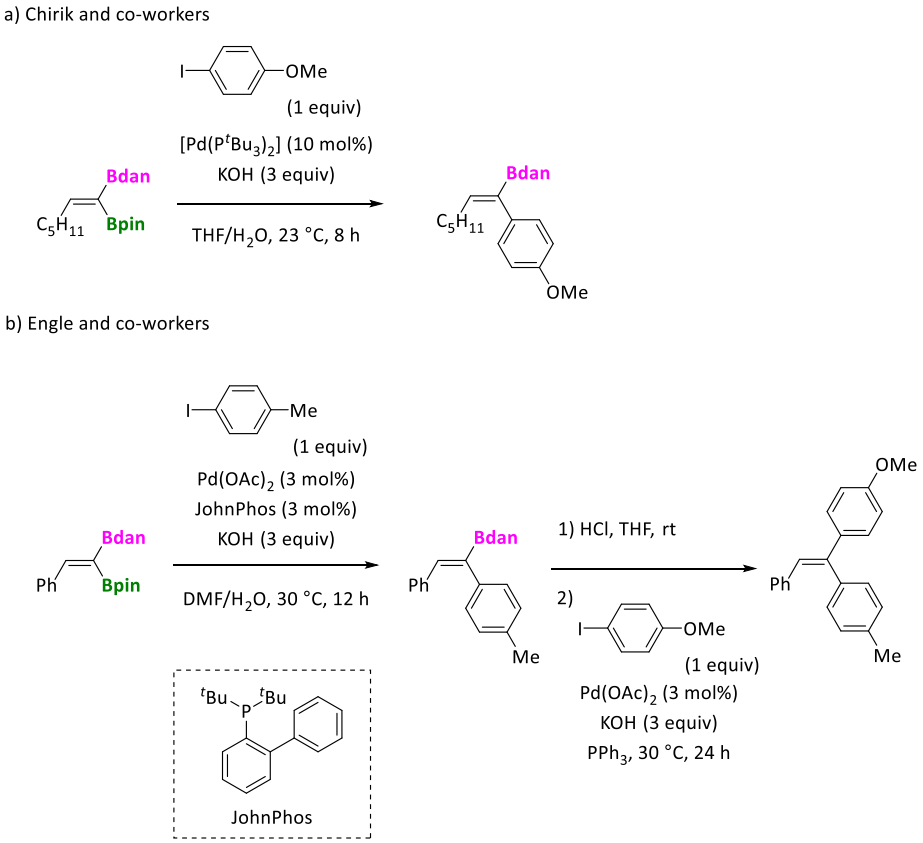


Scheme 1.15. Chemoselective activation of 1,1-diborylalkenes by a) Rh-catalysed conjugate addition and b) Cu-catalysed conjugate addition.

1.3.2. Unsymmetrical *gem*-diborylalkenes

The different reactivity of the two boryl substituents in 1,1-diborylalkenes when both boryl moieties were different, such as Bpin and Bdan, enabled selective Suzuki–Miyaura cross-coupling at the Bpin moiety through stepwise dual C–B bond transformations. In this context, Chirik and co-workers reported the selective Suzuki-Miyaura cross-coupling of 1,1-diborylheptene containing Bpin and Bdan moieties with 4-iodoanisole.[6] The cross-coupling took place on the Bpin moiety due to its higher reactivity compared to the Bdan moiety, resulting in the desired substituted borylalkene with the remaining Bdan group (Scheme 1.16a). Similarly, Engle and co-workers described the sequential cross-coupling reaction of *gem*-diborylalkenes bearing Bpin/Bdan moieties.[22] Using $[Pd(OAc)_2]$/JohnPhos, as the catalytic system, and 4-iodotoluene as the coupling partner, in the presence of KOH, resulted in selective Suzuki-Miyaura coupling at the Bpin moiety (Scheme 1.16b). The subsequent addition

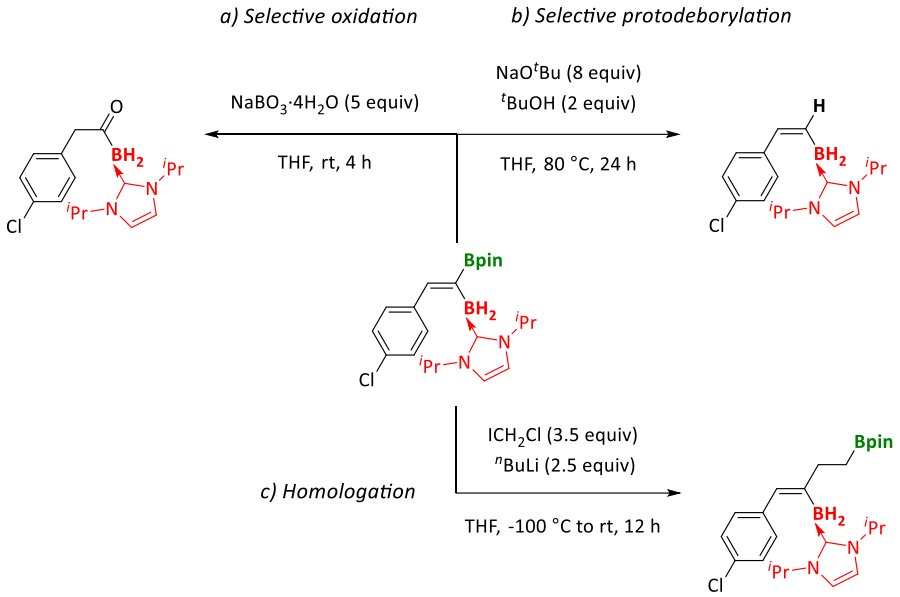
of hydrochloric acid, followed by a catalytic amount of [Pd(OAc)$_2$] and PPh$_3$, 4-iodoanisole, and KOH, allowed the second cross-coupling reaction at the Bdan moiety.



Scheme 1.16. Selective cross-coupling reaction of unsymmetrical *gem*-diborylalkenes at Bpin moiety.

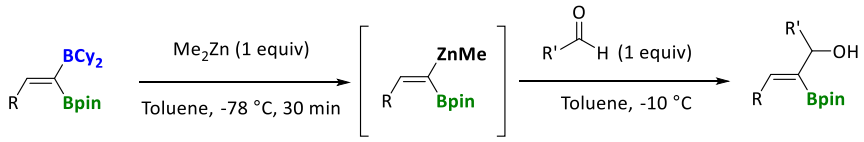
In 2023, Lyu and co-workers reported similar derivatisation of unsymmetrical (NHC)BH$_2$–Bpin *gem*-diborylalkenes.[8] They hypothesised that the coordinatively unsaturated Bpin moiety would be more reactive and thus would be transformed preferentially (Scheme 1.17). To test this hypothesis, they conducted a series of derivatisations, selectively transforming the Bpin moiety while the BH$_2$(NHC) group remained stable. The oxidation afforded the acylborane compound in high yield (Scheme 1.17a). In addition, protodeborylation under basic conditions exclusively yielded the alkene, with only the Bpin group being removed (Scheme 1.17b). This is rationalised by the fact that, compared to the carbene-coordinated sp^3 boryl moiety, the sp^2 Bpin moiety is more susceptible to nucleophilic attack by the base.

Alternatively, they further investigated the Matteson homologation reaction,[23] where the homologated product was formed in moderate yield due to the higher reactivity of C–B(sp^2) bond (Scheme 1.17c).



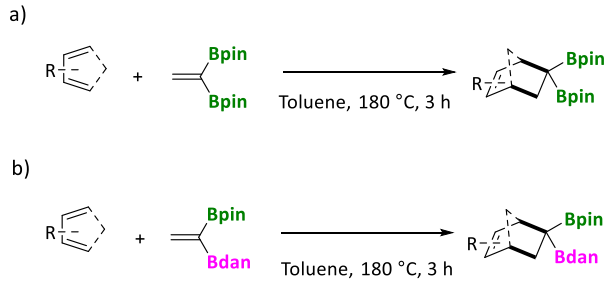
Scheme 1.17. Derivatisation reactions of unsymmetrical (NHC)BH_2–Bpin *gem*-diborylalkene.

Walsh and co-workers investigated the transmetallation of *gem*-diborylalkenes containing Bpin and BCy_2 groups with dimethylzinc (Scheme 1.18).[13] The chemoselectivity observed correlated with the Lewis acid properties of the boryl moieties. Oxygen atoms in Bpin donate electron density to boron, reducing its Lewis acidity. In contrast, cyclohexyl groups donate electron density via σ bonds, which leaves the boron *p* orbital more accessible, thus facilitating the transmetallation process at BCy_2. The resulting heterobimetallic boron/zinc species reacted concurrently with aldehydes to yield the corresponding allylic alcohol products.



Scheme 1.18. Synthesis of allylic alcohols from *gem*-diborylalkenes bearing Bpin/BCy_2 moieties through boron/zinc heterobimetallic intermediates.

In 2021, Masarwa and co-workers demonstrated that symmetrical and unsymmetrical *gem*-diborylalkenes could react with dienophiles for the Diels-Alder cycloadditions.[24] Using the symmetrical *gem*-diborylalkenes, the authors afforded a wide range of cycloaddition products with different functional groups in a regioselective fashion (Scheme 1.19a). In addition, the reaction exhibited moderate regioselectivity when unsymmetrical dienes were used (Scheme 1.19b).



Scheme 1.19. Diels-Alder cycloaddition reaction of 1,1-diborylalkenes.

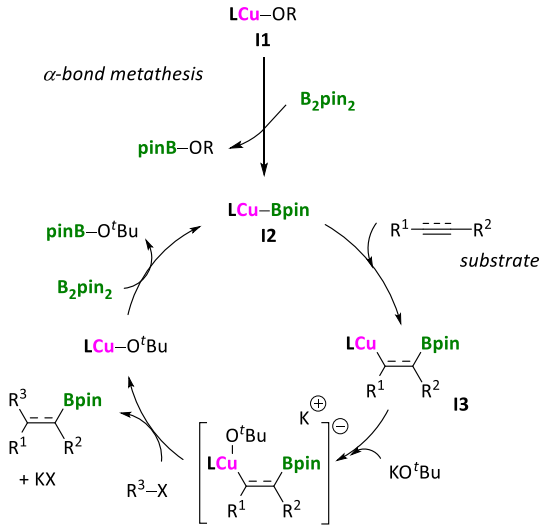
1.4. Borylation of alkenes via copper(I) catalysis

The borylation of the π-system represents a remarkable versatile method for installing new functionalities. In this context, copper complexes have proved to be effective catalysts to introduce boron atom into π-unsaturated systems. Copper(I) and copper(II) enhance the nucleophilicity of boryl moieties to be used under homogeneous catalytic conditions.[25]

One of the earliest report about the use of copper-boryl complexes in synthesis, described the conjugate additions of a Bpin group to an enone by Miyaura and Hosomi in 2000.[26,27] They used either a CuCl/KOAc catalyst or a copper(I) phosphine catalyst in combination with a diboron reagent, suggesting the *in situ* formation of Cu–Bpin fragments to be used in the catalysed β-borylation of α,β-enones.

The organic synthesis promoted by copper-boryl intermediates has attracted enthusiasm for developing several reactions including hydroboration, carboboration, diboration, and heteroboration with unsaturated substrates of multiple bonds. The general mechanism for copper-catalysed borylation of unsaturated substrates has

been suggested to proceed through initial Cu–B bond formation via σ-bond metathesis, between diboranes reagents and Cu–OR, followed by coordination of the π-systems with the concomitant 1,2-insertion to form the C–B bond and the C–Cu bond, which eventually react with an electrophile to generate the corresponding product (Scheme 1.20).[28,29]

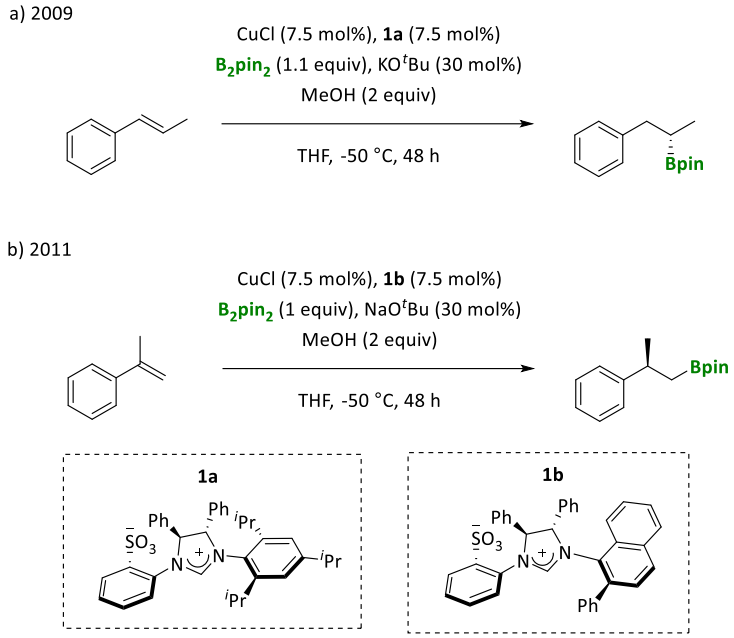


Scheme 1.20. General catalytic cycle for copper-catalysed borylative difunctionalisations.

1.4.1. Hydroboration of alkenes

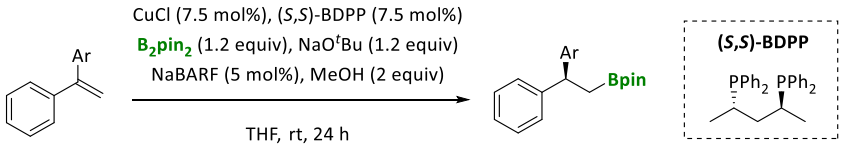
The first reported cases of regio- and enantioselective hydroboration reaction involved 1,2-disubstituted (1-alkyl-2-aryl) alkenes and bis(pinacolato)diboron, catalysed by the (NHC)–Cu complex derived from sulfonate-containing imidazolinium salt **1a** by Hoveyda and co-workers in 2009 (Scheme 1.21a).[30] These reactions were effective with both acyclic and cyclic alkenes, producing the desired boronates with high efficiency and enantioselectivity, although they required prolonged reaction times and cryogenic conditions.

The same authors reported later that the modification of the chiral NHC ligand **1b**, allowed high enantioselectivity in hydroboration reaction of acyclic and exocyclic 1-aryl-1-alkyl olefins (Scheme 1.21b).[31] This type of substrates was particularly challenging for attaining high enantioselectivity through catalytic processes.



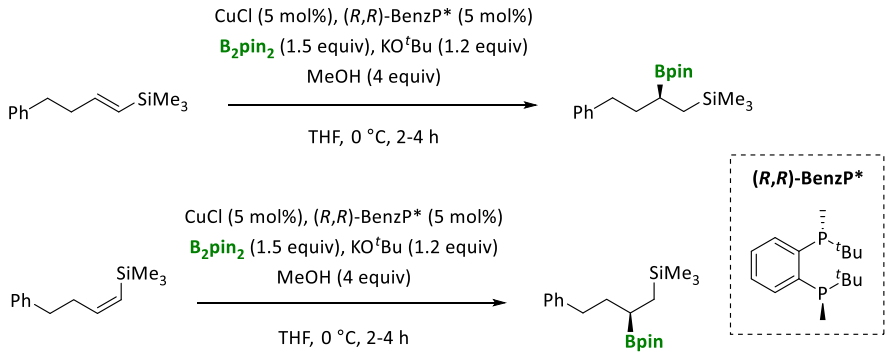
Scheme 1.21. Copper-catalysed hydroboration of alkenes.

Bisphosphine–Cu complexes could also facilitate enantioselective hydroboration to 1,1-disubstituted aryl olefins, such as 1-aryl-1-alkyl and 1,1-diaryl variants (Scheme 1.22).[32] Similar to the reactions involving 1,1-disubstituted substrates (Scheme 1.21), high enantioselectivity was only achieved when the alkenyl substituents differed significantly in size. These reactions took place under ambient conditions and resulted to be more reactive than those using sulfonate-containing NHC ligands (i.e., at room temperature for 24 hours versus –50 °C for 48 hours).



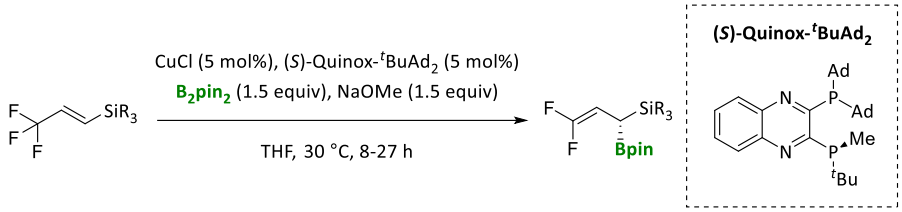
Scheme 1.22. Copper-catalysed hydroboration of 1,1-disubstituted alkenes.

Alternatively, enantioselective hydroboration of (*E*)-alkenylsilanes was conducted generating the corresponding 1,2-borylsilyl organocompounds.[33] In this context, Ito and co-workers reported a hydroboration reaction catalysed by the Cu-based complex derived from relatively electron-rich biphosphine ligands (Scheme 1.23).[34] Depending on the alkenylsilane used, the complementary enantiomer was afforded.



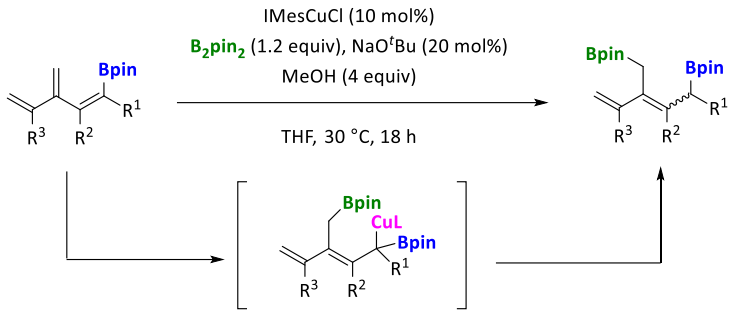
Scheme 1.23. Copper-catalysed hydroboration of alkenylsilanes compounds.

In 2022, the same authors described a copper-catalysed enantioselective borylation of trifluoromethyl- and silyl-substituted alkenes using a QuinoxP*-type bisphosphine ligand to prepare enantioenriched *gem*-difluoro-1-silylallylboronates (Scheme 1.24).[35] The mechanism proceeded with the formation of a borylcopper(I) intermediate and the desired product was obtained via a rapid β-fluoroelimination step.



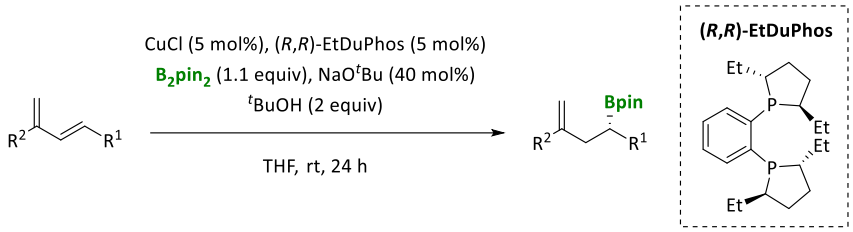
Scheme 1.24. Copper-catalysed of trifluoromethyl- and silyl-substituted alkenes.

Fañanas-Mastral and co-workers reported an efficient hydroboration pathway for borylated dendralenes, using an NHC-Cu catalyst (Scheme 1.25).[36] This method allowed the synthesis of functionalised diborated products with high chemo-, regio-, and stereoselectivity, achieving yields over 95%, under optimised conditions. The (*Z*)-configured diene bis(boronate) was obtained through rapid protonation with CH_3OH and concomitant regeneration of copper alkoxide.



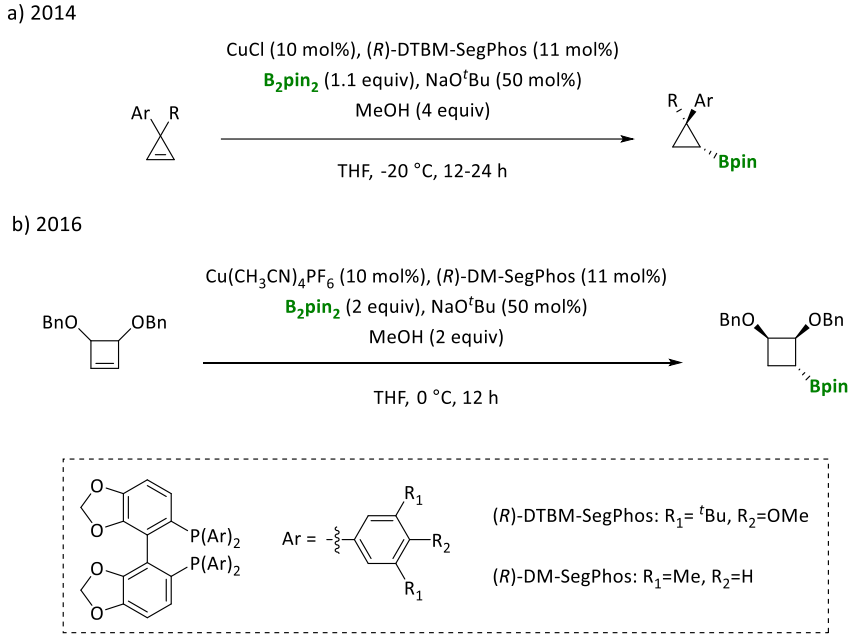
Scheme 1.25. Copper-catalysed hydroboration of borylated dendralenes.

Alternatively, Diver and co-workers explored a regio- and enantioselective Cu-catalysed hydroboration of 1,3-disubstituted-1,3-dienes (Scheme 1.26).[37] The enantioselective reaction was achieved using a chiral ligand (EtDuPhos), while a diphosphine ligand, 1,2-bis(diphenylphosphino)benzene (dppbz), was used in achiral reactions. Based on mechanistic studies, the authors proposed that the reaction proceeded through an allylic copper intermediate. Their model for regioselectivity suggested that the addition of Cu–B to the 1,3-diene favoured the 1,2-addition mode, since steric effects in the 3,4-addition were more severe.



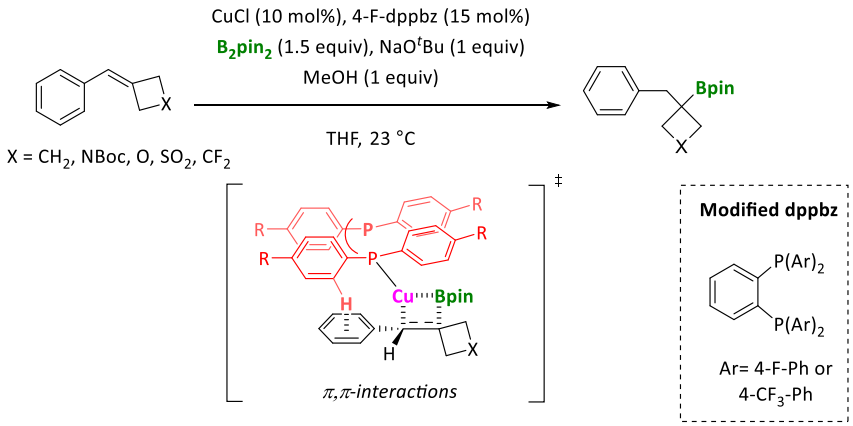
Scheme 1.26. Copper-catalysed enantioselective hydroboration of disubstituted 1,3-dienes.

Tortosa and co-workers described a novel copper-catalysed desymmetrisation of cyclopropenes through hydroboration reaction allowing the synthesis of enantiomerically enriched cyclopropylboronic esters (Scheme 1.27a).[38] In addition, they also studied the desymmetrisation of meso-cyclobutylboronic esters to prepare chiral cyclobutanes, catalysed by a chiral phosphine-copper(I) complex (Scheme 1.27b).[39] Both studies provided access to a wide range of compounds with two and three stereogenic centers, respectively, in high yields and stereocontrol.



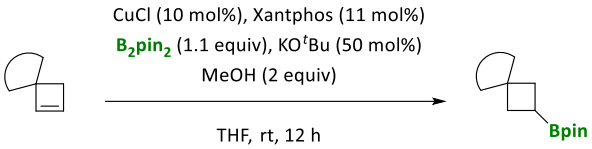
Scheme 1.27. Copper-catalysed desymmetrisation reaction of a) cyclopropylboronic esters and b) cyclobutylboronic esters.

McAlpine, Liu, Engle, and co-workers developed a copper-catalysed hydroboration method for various trisubstituted benzylidenecyclobutanes, producing synthetically useful tertiary boronic ester products (Scheme 1.28).[40] They proposed that ligands such as 4-F and 4-CF_3-dppbz facilitate T-shaped π/π interactions between themselves and the substrate. The reactivity was primarily influenced by bond interactions between the catalysts and substrates with different electronic properties.



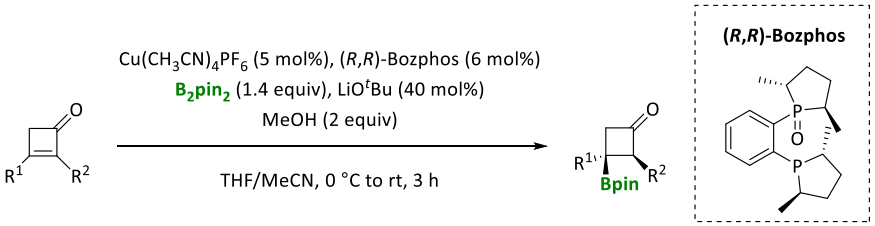
Scheme 1.28. Copper-catalysed hydroboration of benzylidenecyclobutanes.

In 2021, Tortosa and co-workers reported a CuCl-catalysed regioselective hydroboration of spirocyclobutenes at room temperature (Scheme 1.29).[41] Using commercially available Xantphos and a CuCl catalyst, they achieved a wide variety of borylated spirocycles with complete regiocontrol, incorporating different functional groups into the borylated spirocyclic framework.



Scheme 1.29. Regioselective hydroboration of spirocyclobutenes.

Oestreich and co-workers identified a chiral bis(phosphine) monoxide (BPMO) ligand that significantly enhanced the asymmetric induction in the copper-catalysed conjugated hydroboration of α,β-cyclobutenones to afford tertiary borylated cyclobutanones (Scheme 1.30).[42] They found that electron-rich substituents like *tert*-butyl and methoxy groups decreased the diastereoselectivity of the target molecule. Conversely, electron-withdrawing groups such as CF_3 and esters yielded the desired products with high enantioselectivities.



Scheme 1.30. Copper-catalysed hydroboration of α,β-cyclobutenones.

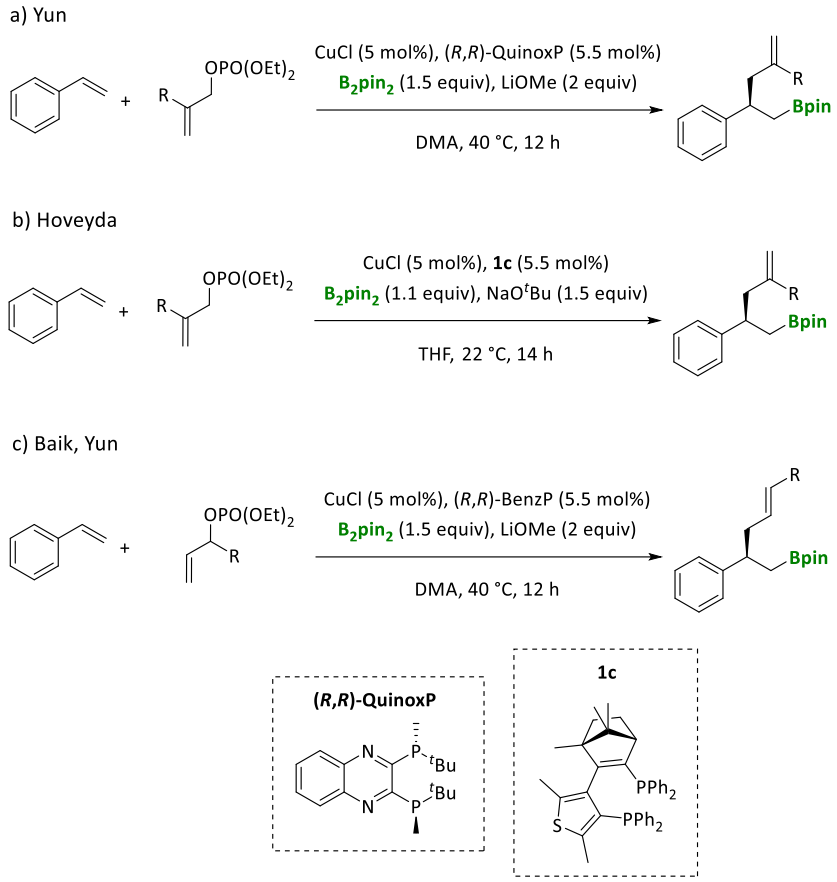
1.4.2. Carboborylation of alkenes

The installation of different functional groups along C–C unsaturated bonds, in a single process, is a powerful method to prepare complex organic molecules. In recent years, organocopper intermediates generated by borylcupration of unsaturated substrates, with bis(pinacolato)diboron, facilitated the formation of various C–C bonds through addition, substitution, and coupling reactions with electrophiles.

A copper-catalysed, enantioselective method for the borylallylation of vinyl arenes was reported by Yun and co-workers (Scheme 1.31a).[43] This reaction produced enantioenriched and functionalised organoboron compounds by sequential addition of boryl and allyl groups to the C=C bond of vinyl arenes. The copper-catalysed borylative coupling of vinyl arenes with allyl phosphates proceeded successfully in a regio- and enantioselective manner, without the need of a palladium co-catalyst. Additionally, 1,2-disubstituted aryl olefins were not transformed under these conditions, due to competitive side reactions between the *in situ* generated copper-boryl complex and the allyl phosphate.

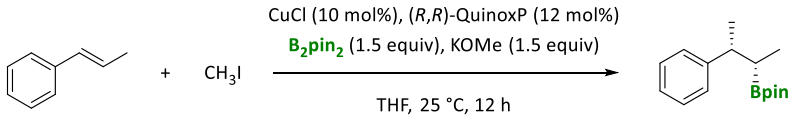
A subsequent, more in-depth study revealed that with a better understanding of mechanistic steps, it was possible to identify conditions that promote highly efficient and enantioselective allyl-boryl additions using a single catalyst system (Scheme 1.31b).[44] By employing a single Cu-based complex, generated *in situ* with a bisphosphine ligand **1c**, the highly regio- and enantioselective allyl-boron additions to both electron-rich and electron-deficient aryl alkenes were achieved.

More recently, Baik, Yun, and co-workers described a Cu-catalysed stereoconvergent coupling reaction between vinyl arenes and racemic acyclic allyl phosphates with B_2pin_2 (Scheme 1.31c).[45] Additionally, the authors examined the scope of vinyl (hetero)arenes and 2-allylic phosphates bearing alkyl and phenyl substituents, achieving the expected products with enantioselectivities as high as 95% ee.



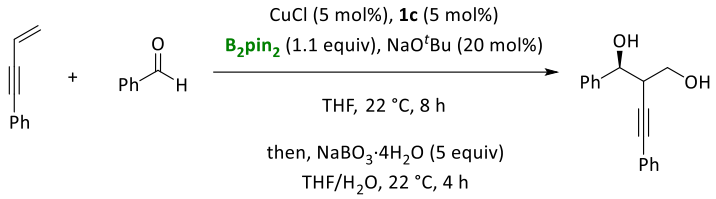
Scheme 1.31. Copper-catalysed allylation reaction.

In addition to allyl electrophiles, methyl iodide has been used in copper-catalysed alkyl-boryl additions to vinylarenes using QuinoxP as a ligand (Scheme 1.32).[46] In these transformations, alkenes including styrenes, β-substituted styrenes, and aliphatic olefins were transferred to the desired methylboration products with good diastereoselectivities and enantioselectivities, although yields were lower for the acyclic (*Z*)-alkene isomers.



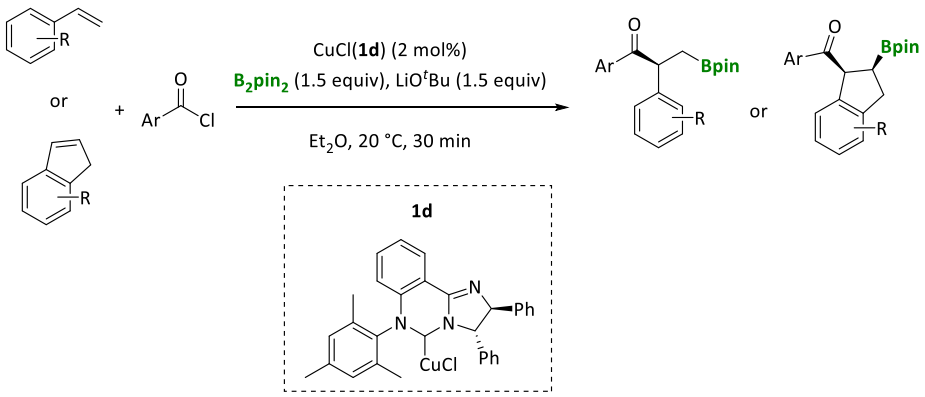
Scheme 1.32. First example of enantioselective Cu-catalysed methylboration of alkenes.

Enantioselective catalytic carboborylation reaction involving carbonyl-containing compounds or imines were first reported by combining a 1,3-enyne, bis(pinacolato)diboron, and an aldehyde by Hoveyda and co-workers (Scheme 1.33).[47] These reactions utilised a chiral bisphosphine–Cu complex, yielding homopropargylic 1,3-diols with high diastereo- and enantioselectivities. A wide range of aryl-, alkenyl-, and alkyl-substituted aldehydes are suitable substrates. Additionally, 1,3-enynes bearing aryl, alkenyl, or silyl-protected alkyne groups could be converted to the desired products with similarly high efficiency and enantioselectivity.



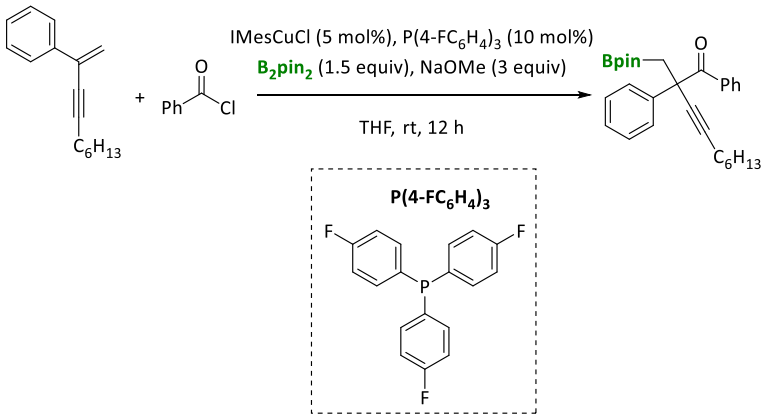
Scheme 1.33. Cu-catalysed carboborylation reaction with aldehydes.

In 2021, Lu and Li and co-workers reported a copper-catalysed reaction for adding boryl groups selectively to aryl olefins using acyl chlorides and bis(pinacolato)diboron (Scheme 1.34).[48] This three-component reaction involved an enantioselective *syn*-borylcupration of the aryl olefin, followed by a nucleophilic attack on the acyl chloride. Furthermore, the process was amenable to scale-up, and the resulting β-borylated ketones were versatile intermediates capable of undergoing multiple subsequent transformations.



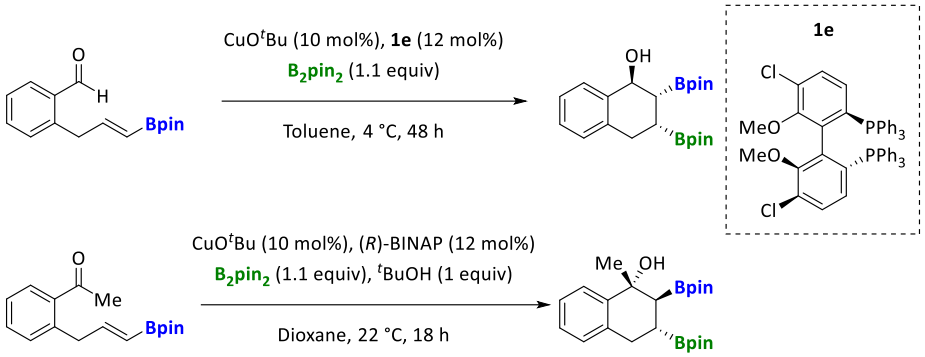
Scheme 1.34. Cu-catalysed asymmetric borylacylation of styrene and indene compounds.

In this context, Zhang, Peng, and co-workers studied the copper-catalysed 1,2-borylacylation of 1,3-enynes using B_2pin_2 and acid chlorides (Scheme 1.35).[49] Following the screening of various ligands, they achieved favourable outcomes employing a $P(4\text{-}FC_6H_4)_3$ ligand. The reaction enabled the synthesis of a variety of highly functionalised α,α-disubstituted β-alkynyl ketones under mild conditions, yielding moderate to good yields with high regioselectivity. Additionally, the authors demonstrated that treatment of the products with $NaBO_3{\cdot}4H_2O$ afforded 1,2-allenyl ketones, likely proceeding through a retro-aldol process of the corresponding homopropargyl alcohols. They proposed that the reaction proceeds via a borylated allenyl-copper intermediates, based on the previous research of Hoveyda and co-workers.[47]



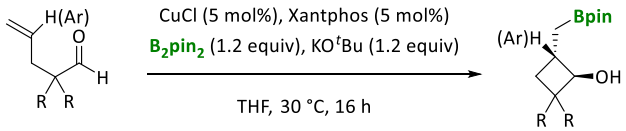
Scheme 1.35. Cu-catalysed asymmetric borylacylation reaction.

Vinyl boronates constitute another significant type of substrate used in the development of catalytic carboborylation processes. An intramolecular strategy of this transformation, resulting in the formation of carbocyclic alcohols, was studied by Meek and co-workers (Scheme 1.36).[50] These transformations involving aldehydes generally yielded lower compared to ketones. This was attributed to competitive 1,2-copper–boryl addition. Furthermore, the authors suggested that aldehydes underwent direct stereoretentive Cu-alkyl addition, while sterically more hindered ketones proceeded through a stereoinvertive pathway, yielding different diastereomers.



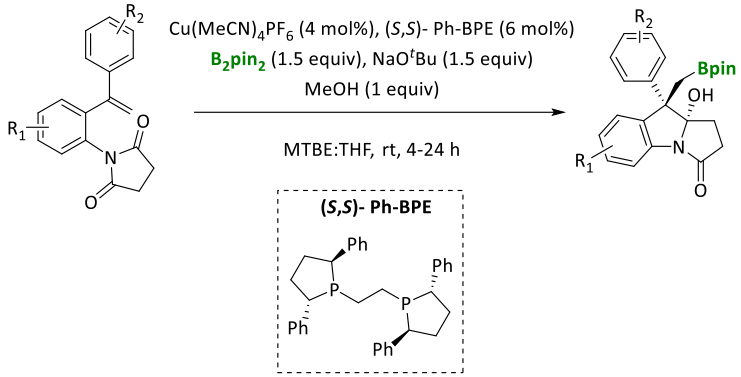
Scheme 1.36. Cu-catalysed intramolecular carboborylation reaction.

More recently, Carbó, Fernández, and co-workers reported a copper-catalysed borylative ring-closing of unactivated alkenes with electrophilic sites involving a strategic intramolecular 1,2-carboborylation process (Scheme 1.37).[51] They developed a copper(I)-catalysed borylative cyclisation method to synthesise *anti*-diastereoselective 2-(borylmethyl)cycloalkanols using α-alkenyl aldehydes as the starting materials. This reaction proceeded through a regioselective boryl addition to the C=C bond, followed by an intramolecular 1,2-addition of the Cu-C bond to the C=O bond.



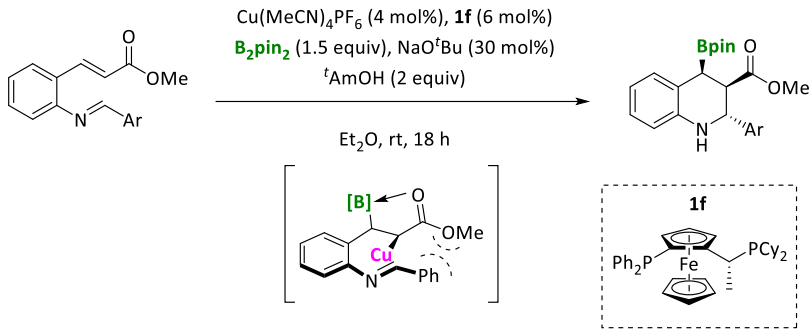
Scheme 1.37. Cu-catalysed borylative ring closing reaction.

For the synthesis of chiral borylated β-lactams, Lautens and co-workers developed an enantioselective copper-catalysed borylation/1,2-imide addition cascade to assemble boron-containing indolines (Scheme 1.38).[52] This work showcased the effectiveness of copper catalysis in constructing complex boron-containing heterocycles and introduced a novel method for synthesising biologically relevant indolines. The asymmetric borylacylation of 1,1-disubstituted alkenes was optimised to proceed via an (*S*)-configured benzyl-copper intermediate, forming a chiral borylated β-lactam ring through cyclisation of the benzyl-copper intermediate.



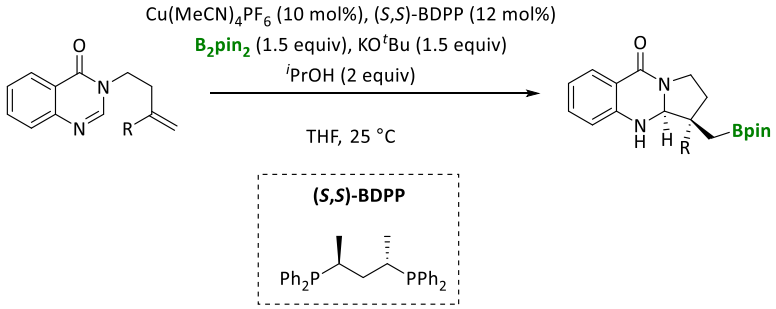
Scheme 1.38. Cu-catalysed borylation/1,2-imide addition reaction.

In 2021, Lautens and co-workers documented a protocol for synthesising enantioenriched *N*-heterocycles through a copper-catalysed conjugate borylation or Mannich cyclisation (Scheme 1.39).[53] This catalytic system was easy to handle, scalable, and capable of creating complex *N*-heterocycles with stereocenters. Moreover, various Michael acceptors demonstrated the broad applicability of this method.



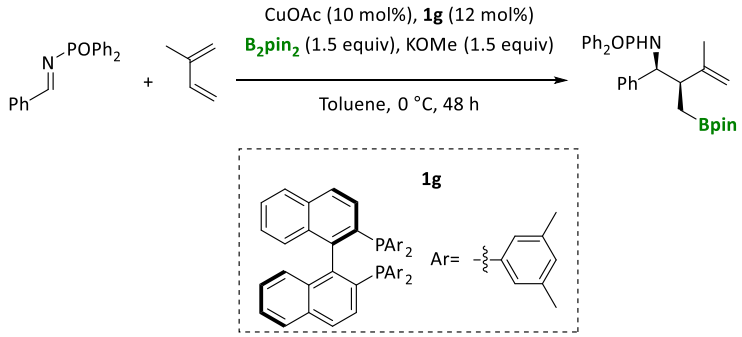
Scheme 1.39. Cu-catalysed sequential 1,4-borylation/Mannich cyclisation reaction.

The same year, Procter and co-workers reported the enantioselective synthesis of pyrroloquinazolinone via copper-catalysed borylative cyclisation reaction (Scheme 1.40).[54] The reaction used an affordable, non-toxic copper catalyst and readily available chiral phosphine ligands. This strategy enabled the efficient processing of various aryl-substituted alkenes, delivering pyrroloquinazolinones with good to excellent enantio- and diastereo-control.



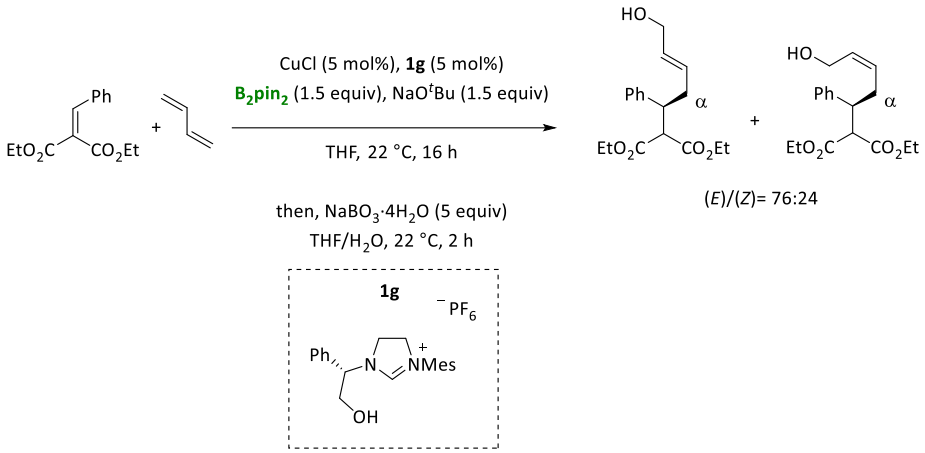
Scheme 1.40. Cu-catalysed borylative cyclisation for the synthesis of quinazolinones.

Another significant catalytic carboborylation process involved combining a 2-substituted-1,3-diene, bis(pinacolato)diboron, and *N*-Dpp aldimines (Scheme 1.41).[55] After oxidation, the desired 1,3-amino alcohols were obtained with high diastereo- and enantioselectivities. However, alkyl-substituted aldimines are less effective, likely due to lower substrate stability.



Scheme 1.41. Cu-catalysed enantioselective borylative aminoalkylation of isoprene.

Alternatively, enantioselective Cu–B addition to activated alkenes followed by 1,4-conjugate addition was studied by Hoveyda and co-workers using an (NHC)-Cu complex, feedstock butadienes and α,β-unsaturated carbonyl compounds (Scheme 1.42).[56] The resulting alcohol products are primarily α-addition isomers with moderate *E*/*Z* ratios but high enantioselectivities.



Scheme 1.42. Cu-catalysed enantioselective conjugate addition reaction.

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Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

CHAPTER II

Objectives

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Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

Objectives

The present doctoral thesis has been focused to develop new chemical methodologies through organoboron compounds. The specific objectives of the different chapters are described below:

We aimed to explore the C(sp^2)–B/B'–B' cross-metathesis transborylation reaction between stable alkenyl boronic esters with both symmetric and non-symmetric diboron reagents.

We also focused on the study of palladium-catalysed insertion of (trimethylsilyl)diazomethane into symmetrical and non-symmetrical *gem*-diborylalkenes with a particular emphasis on the stereoselectivity of the cyclopropanation reaction.

We searched on the copper(I)-Xantphos system to catalyse the regioselective borylcupration of borylated skipped (*Z*)-dienes generating diborylated alkylcopper species. We aimed to induce a stereospecific B/Cu 1,3-rearrangement through remote boron shift from C(sp^2) to C(sp^3). Subsequent applications searched a direct synthesis of alkylidene cycloalkanes.

We aimed to study the reactivity of a remote carbon-to-carbon boryl migration based on a 1,4-B/Cu shift. The synthetic application has searched the preparation of functionalised cyclopentenes through a palladium-catalysed regioselective intramolecular coupling that was susceptible of strategic cyclopropanation to generate valuable structural bicyclic systems.

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CHAPTER III

Transborylation reaction of alkenylboranes with diboron reagents

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Paula Dominguez Molano

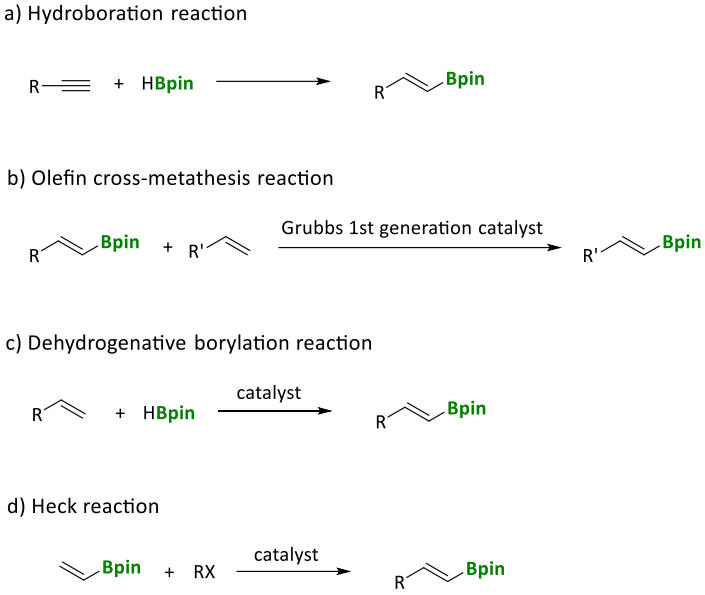
3.1. State of the art

One of the most relevant goals in the organic synthetic community is the accessibility to functionalised molecules.[1] In this framework, alkenylboranes have emerged as powerful intermediates for the functionalisation of alkenes, as it has been demonstrated in recent decades.[2,3] Specifically, (*E*)-alkenylboranes have become essential building blocks for developing functionalised alkenyl groups while maintaining stereoselectivity. This is attributed to the inherent versatility of the C−B bond, which enables selective functionalisation at subsequent stages of synthesis. The synthesis of both (*E*)- and (*Z*)-alkenylboranes has been described using innovative methodologies. This chapter is focused on the accessibility to alkenylboranes with emphasis on the transborylation reaction.[4,5]

3.1.1. Synthesis of (*E*)-alkenylboranes

The hydroboration of alkynes is the most extended approach for synthesising (*E*)-alkenylboranes. This method relies on the *syn* addition of the boron-hydrogen bond to the carbon-carbon triple bond.[6,7] Brown's pioneering research prompted the advancement of this field, leading to the development of various methodologies −both metal-catalysed and metal-free− for the conversion of alkynes into alkenylboranes in a regioselective manner (Scheme 3.1a). Alternatively, an olefin cross-metathesis reaction has been applied for the preparation of alkenyl boronates in the presence of Grubbs' first-generation catalysts (Scheme 3.1b).[8] Another approach for synthesising (*E*)-alkenylboranes involved dehydrogenative borylation of alkenes, primarily catalysed by rhodium complexes,[9] although palladium,[10] iron,[11] cobalt,[12] or copper[13] could also be employed for catalysing this transformation (Scheme 3.1c).

Eventually, the palladium-catalysed Heck coupling of alkenylboranes with (het)aryl halides has been revealed to proceed with significant stereoselectivity, favouring the (*E*)-stereoisomer (Scheme 3.1d).[14] As an extension, it has been described an alternative procedure by the palladium catalysed Heck reaction between terminal alkenes and catecholchloroborane.[15]

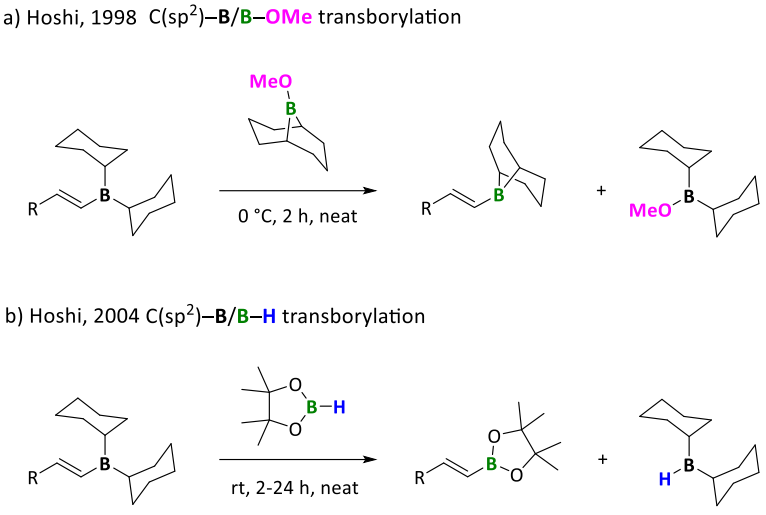


Scheme 3.1. Complementary strategies towards (*E*)-alkenylboranes.

3.1.2. Transborylation reaction of alkenylboranes

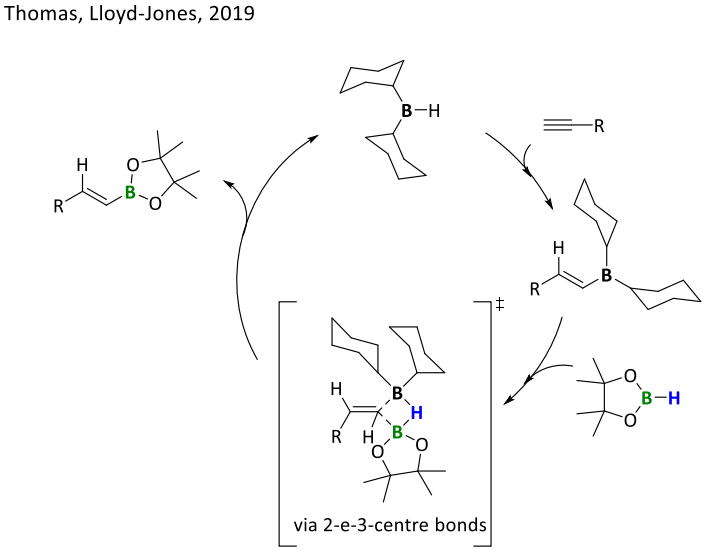
A new synthetic strategy towards alkenylboranes formation was based on the transborylation pathway. Transborylation could be defined as a controlled boron-boron exchange.[16]

In 1998, Hoshi and co-workers developed the first example of alkenyl group transfer from boron to boron, in stoichiometric amounts, by σ-bond metathesis pathway, in the absence of metal catalysts.[17] They proved that (*E*)-alkenyl dicyclohexylborane reacted smoothly at 0 °C with 9-methoxy-9-borabicyclo[3.3.1]nonane (9-MeO-9-BBN). This exchange of boryl moieties was conducted for a synthetic utility under mild conditions, preserving configuration entirely through the cleavage of stable boron-oxygen bond in B-MeO-9-BBN through C(sp^2)−B/B−H transborylation sequence (Scheme 3.2a). The authors revealed an alternative method for synthesising 1-alkenyl pinacolborane compounds by transferring the alkenyl group from dicyclohexylborane (BCy_2) to pinacolborane.[18, 19] This approach retained the original (*E*)-stereoselectivity, as depicted in Scheme 3.2b.



Scheme 3.2. Efficient pathways through transborylation reactions.

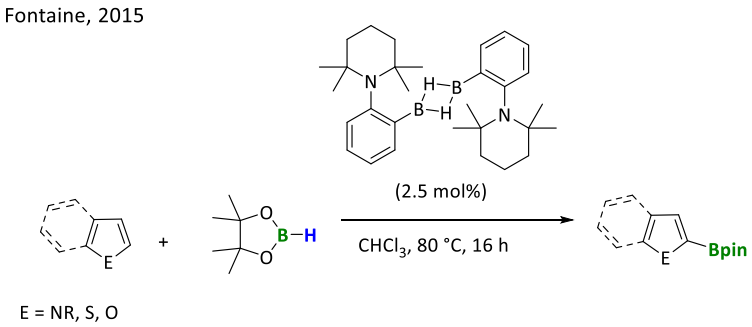
Motivated by the lack of fundamental understanding of these transformations, the mechanism of the transborylation between C(sp^2)–B and B–H has been deeply studied by Thomas, Lloyd-Jones, and co-workers.[20, 21] They demonstrated that transborylation between (*E*)-alkenylboranes and HBpin involved a μ–B–H–B bridged, 2-electron-3-center transition state (Scheme 3.3).



Scheme 3.3. Mechanistic proposal for transborylation reaction.

Inspired by these findings, they explored the alkyne hydroboration catalysed by commercially available 9-borabicyclo[3.3.1]nonane dimer $(9\text{-BBN})_2$ as an alternative to the air-sensitive $(Cy_2BH)_2$ suspension. The outcomes revealed a comparable array of intermediates to those identified in the Hoshi hydroboration reaction.

In 2015, Fontaine and co-workers studied the metal-free C–H functionalisation of heteroarenes with boranes.[22] They demonstrated that boranes could activate the C–H bonds of heteroarenes by intramolecular frustrated Lewis pair (FPLs) formation allowing the C–H bond cleavage and subsequent dehydrogenative borylation of heteroarenes without the need for noble metals. This achievement represents an important breakthrough in the metal-free hydroboration reaction. Dimer $(TMP\text{-}2\text{-}BH_2\text{-}C_6H_4)_2$ (TMP = 2,2,6,6-tetramethylpiperidine) was the candidate to activate the $C(sp^2)$–H of the heteroarene, as depicted in Scheme 3.4. 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 species.

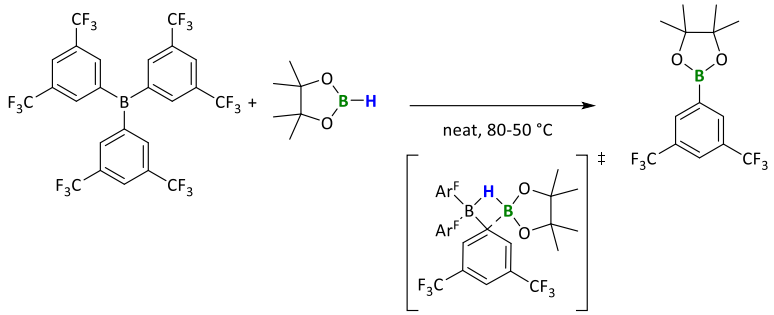


Scheme 3.4. Postulated σ-bond metathesis in $C(sp^2)$–B/B–H transborylation.

Transborylation of alkenylboranes with diboron reagents

A similar σ-bond metathesis exchange has been suggested by Oestreich and coworkers for transborylation between tris(3,5-bis(trifluoromethyl)phenyl)borane (BAr_3^F) and pinacolborane, although a higher temperature (up to 80 °C) is required (Scheme 3.5).[23]

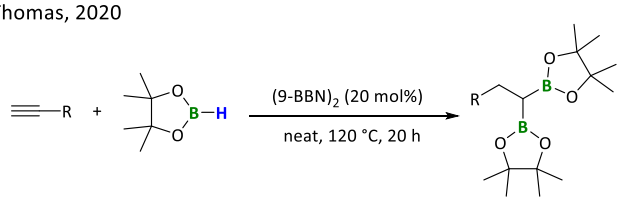
Oestreich, 2016



Scheme 3.5. First example of C(sp^2)–B/B–H transborylation with aryl groups.

More recently, Thomas and co-workers have reported a double transborylation strategy for synthesising *gem*-diborylalkanes, using reagent 9-borabicyclo[3.3.1]nonane dimer $(9\text{-BBN})_2$, as a catalyst and pinacolborane as the transborylative reagent.[21] Their investigations suggested a proposed mechanism where borane-catalysed alkyne hydroboration, followed by C(sp^3)–B/B–H transborylation reactions, yields the versatile and stable *gem*-diborylalkane compound, as outlined in Scheme 3.6.

Thomas, 2020



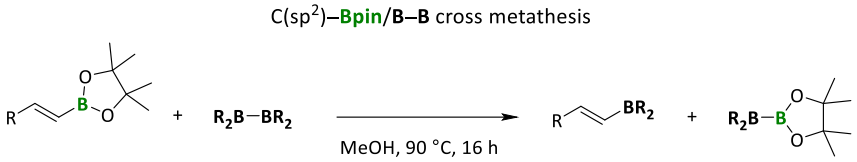
Scheme 3.6. Model reaction for borane-catalysed double transborylation.

3.2. Project aims

The main objective of this project is to study the transborylation reaction between stable (*E*)-alkenylboranes, containing the C(sp^2)–Bpin fragment, and diverse diboron reagents (Scheme 3.7).

The specific objectives are:

- Explore the stereospecific transborylation reaction with (*E*)-1,2-, (*Z*)-1,2-, 1,1-, and 1,1,2-substituted alkenylboranes.
- Study the general application of symmetric and non-symmetric diboron reagents, as well as the formation of the corresponding diboron by-products.
- Launch a mechanistic spectroscopic study to understand the transborylation pathway.

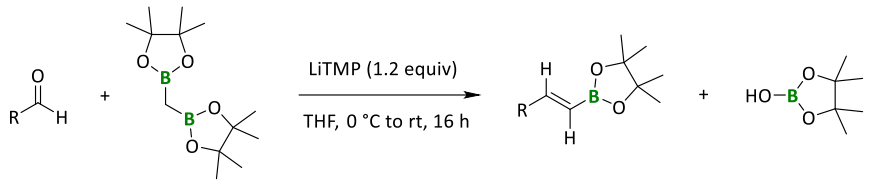


Scheme 3.7. Application of C(sp^2)–Bpin/B–B transborylation reaction.

3.3. Results and discussion

3.3.1. Synthesis of alkenyl pinacolboranes

The investigation was initiated by synthesising a series of alkenyl pinacolboranes, through a boron-Wittig olefination reaction (Scheme 3.8).[24] The boron-Wittig reaction with *gem*-diborylalkanes resembles the Wittig olefination based on the formation of alkenes by the reaction of aldehydes or ketones with ylides generated from phosphonium salts. The driving force of Wittig olefination was commonly associated with the formation of a very stable phosphine oxide, whereas in the boron-Wittig transformation, the driving force was due to the stability associated with the formation of B–O bonds in pinacolboronic acid.

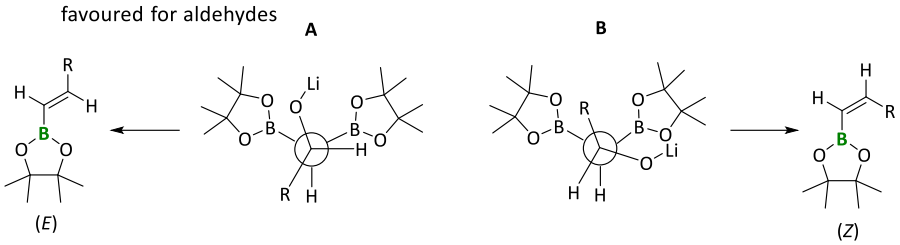


Scheme 3.8. Synthesis of (*E*)-alkenylboranes through boron-Wittig olefination reaction. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

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.

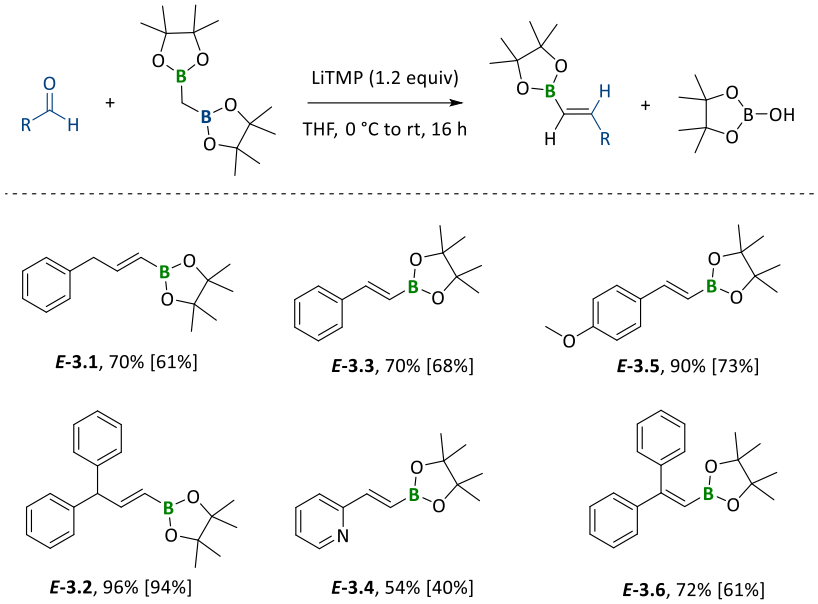
In 2015, Morken and co-workers reported a stereoselective boron-Wittig olefination between bis(pinacolboryl)methanes, lithium salts, and aldehydes, obtaining a variety of synthetically useful (*E*)-alkenylboranes with an *E*/*Z* ratio of 97/3, at room temperature.[25]

On the other hand, a similar preferred formation of (*E*)-alkenylboranes was observed by Grygorenko and co-workers under the same conditions.[26] The authors justified the control of (*E*)-stereoselectivity through the conformational models **A** and **B** in Scheme 3.9. It can be seen that in the case of aldehydes, the conformation **A** might be completely favoured versus the conformation **B**.



Scheme 3.9. Suggested models for high stereoselectivity in boron-Wittig reaction with aldehydes.

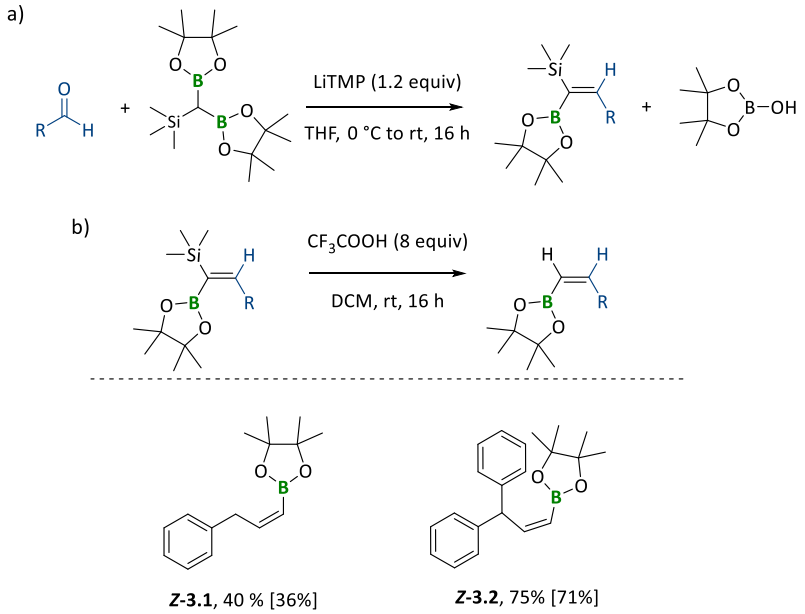
Following this methodology, we have synthesised several (*E*)-1,2-disubstituted boronic esters employing the optimised reaction conditions detailed in the literature (Scheme 3.10). Di- and tri-substituted olefins were isolated in moderate yields with (*E*)-stereoselectivity.



Scheme 3.10. Synthesis of (*E*)-alkenyl pinacolborane compounds. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

The formation of (*Z*)-alkenylboranes was conducted under the conditions reported by Petit and co-workers.[27] This protocol involved 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 to generate the (*Z*)-alkenyl pinacolborane as the exclusive alkene (Scheme 3.11).

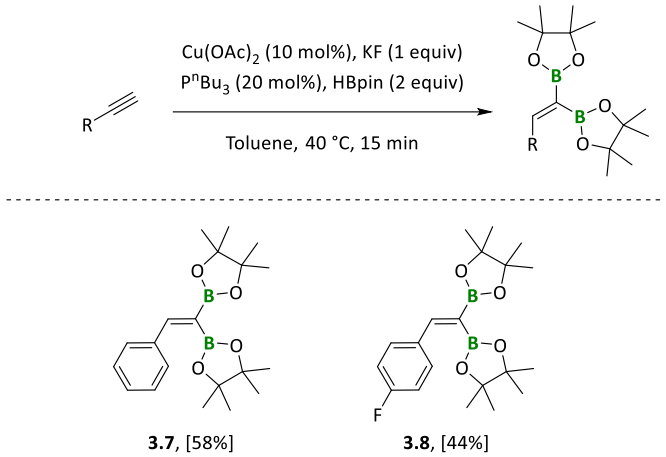


***Z*-3.1**, 40 % [36%] ***Z*-3.2**, 75% [71%]

Scheme 3.11. Synthesis of (*Z*)-alkenyl pinacolborane compounds. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

The synthesis of 2-substituted 1,1-diborylalkenes from easily available terminal alkynes was conducted *via* copper-catalysed dehydrogenative borylation/hydroboration with pinacolborane. Marder and co-workers studied a related reactivity aimed at producing triborylalkanes from terminal alkynes.[28] This reaction involved the dehydrogenative borylation of terminal alkynes followed by double hydroboration to afford the desired tris(pinacolboryl)alkanes. Through mechanistic experiments, they suggested the formation of 1,1-bis(boryl)alkene by using 2 equivalents of HBpin and reducing the reaction time to 6 h. With this precedent in mind, we designed an alternative synthetic methodology to obtain the target 2-substituted 1,1-diborylalkenes. The key factor in the reactivity relied on the reaction time. At the 15-minute mark, the formation of 2-substituted 1,1-diborylalkene started to compete with its reactivity with HBpin towards the triborylated product formation. Consequently, beyond the 15-minute reaction time, we were able to isolate the desired 2-substituted 1,1-diborylalkenes in moderate

yield. However, as illustrated in Scheme 3.12, the yields show a slight improvement compared to Marder's synthesis.[28]



Scheme 3.12. Synthesis of 1,1-diborylalkene compounds. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

Figure 1.1. illustrated the substituted 1-pinacolborylethenes 3.9-3.11 that were obtained from commercial sources, to study the influence of phenyl and methyl functional groups vicinal to 1-pinacolethenes.

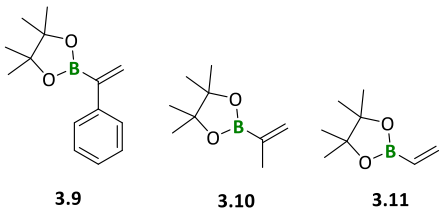


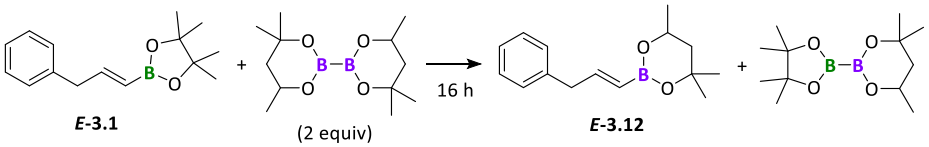
Figure 3.1. Commercially available substituted 1-pinacolborylethenes.

3.3.2. Study of transborylation of alkenyl pinacolboranes

To demonstrate the viability of the C(sp^2)–Bpin/B–B transborylation reaction, we initially assessed the cross-metathesis between (*E*)-1,2-disubstituted boronic ester ***E*-3.1** and bis(hexyleneglycolato)diboron (B_2hex_2) at 90 °C in THF. However, this reaction proved to be inefficient, as substrate ***E*-3.1** remained unaltered after 16 hours of reaction. Surprisingly, the replacement of THF by MeOH allowed the conversion of ***E*-3.1** into the alkenyl boronic ester ***E*-3.12**, from moderate yield at room temperature

to high yield when the reaction was conducted at 90 °C (Table 3.1). Importantly, product ***E*-3.12** retained its (*E*)-configuration from the initial alkenyl pinacolborane substrate, and the formation of the mixed diboron reagent pinB–Bhex was observed as a by-product due to the Bpin/Bhex exchange.

Table 3.1 Optimisation of the reaction conditions for the transborylation reaction.[a]



***E*-3.1** (2 equiv) ***E*-3.12**

ENTRY	SOLVENT	TEMPERATURE (°C)	YIELD[b] (%)
1	THF	90	0
2	MeOH	rt	83% [65%]
3	MeOH	90	91% [89%]

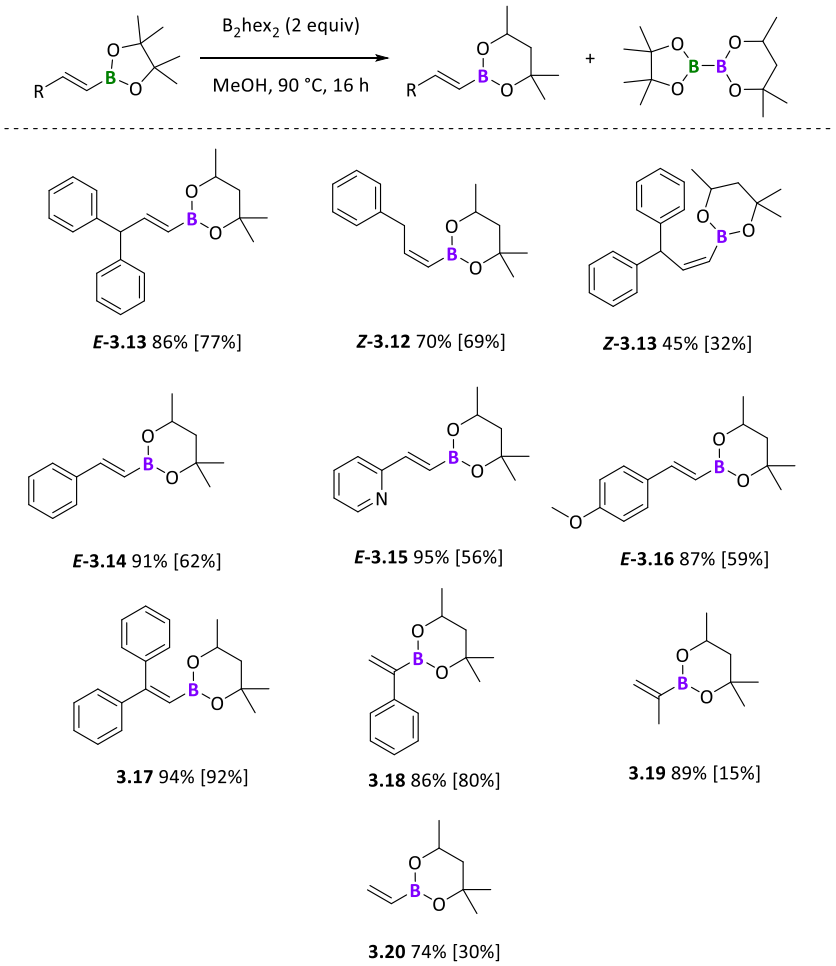
[a]Reactions were performed with 0.3 mmol of model substrate ***E*-3.1** and 0.6 mmol of the diboron reagent in 2 mL of solvent. [b]Yields were calculated from the ^{1}H-NMR using naphthalene as an internal standard. Isolated yields in brackets.

We next examined the transborylation of substrates ***E*-3.2**, ***E*-3.3**, ***E*-3.4**, ***E*-3.5**, and ***E*-3.6** 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*-3.13**, ***E*-3.14**, ***E*-3.15**, ***E*-3.16**, and ***E*-3.17** (Scheme 3.13). Remarkably, the reaction of substrate ***E*-3.3** in THF, adding 1.5 equivalents of MeOH, only transborylated 9% into ***E*-3.14**, confirming the need for MeOH as a solvent.

Since the configuration of the (*E*)-alkenyl pinacolboronate substrates were retained along the transborylation reaction, we next tested the transborylation of (*Z*)-1,2-disubstituted boronic ester ***Z*-3.1** and ***Z*-3.2** with B_2hex_2. Under the optimised reaction conditions, both substrates were successfully converted to their respective transborylated boronic esters ***Z*-3.12** and ***Z*-3.13**, respectively, with total retention of the (*Z*)-configuration. However, the yield for ***Z*-3.13** was lower compared to ***E*-3.13**, likely due to steric hindrance associated with its *cis* configuration (Scheme 3.13).

Transborylation of 1-pinacolborylethenes was next studied and substrate **3.9** was efficiently transborylated with B_2hex_2 in MeOH, isolating 80% of 4,4,6-trimethyl-2-(1-phenylvinyl)-1,3,2-dioxaborinane **3.18** (Scheme 3.13). In addition, we were able to

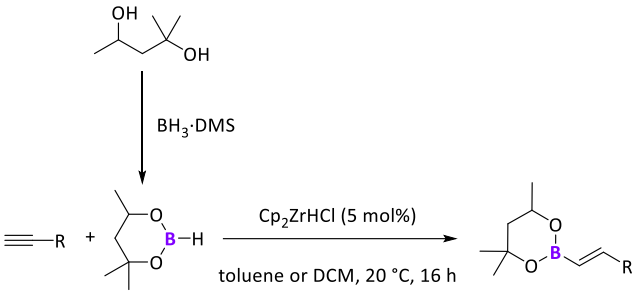
perform the transborylation of 2-pinacolboryl propene **3.10** as well as pinacolboryl ethene **3.11** into the corresponding transborylated products **3.19** and **3.20**, with high conversion. However, isolated yield decreased since both products have low boiling points.



Scheme 3.13. Substrate scope for transborylation of alkenyl pinacolboranes with B_2hex_2. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

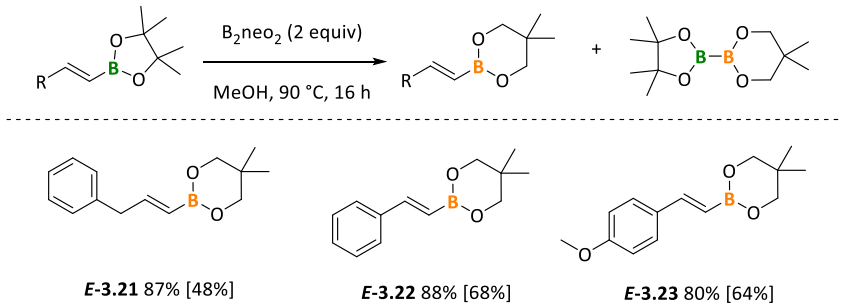
This methodology complemented the reported synthesis of alkenylboranes containing Bhex that were prepared before through Cp_2ZrHCl catalysed hydroboration of terminal alkynes with HBhex.[29] Chavant and co-workers reported that methylpentanediolborane (HBhex) was capable of hydroborate 1-alkynes with

Schwart's reagent, as the catalyst, under mild conditions with retention of the configuration (Scheme 3.14).



Scheme 3.14. Hydroboration of 1-alkynes with HBhex.

We then investigated the transborylation reaction of ***E*-3.1**, ***E*-3.5**, and ***E*-3.6** with bis(neopenthyl glycolato)diboron (B_2neo_2). The exclusive formation of the transborylated (*E*)-alkenyl neopentyl glycolato boronic esters ***E*-3.21**, ***E*-3.22**, and ***E*-3.23** prompted us to examine the broader applicability of this reaction (Scheme 3.15).



***E*-3.21** 87% [48%] ***E*-3.22** 88% [68%] ***E*-3.23** 80% [64%]

Scheme 3.15. Substrate scope for transborylation of alkenyl pinacolboranes with B_2neo_2. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

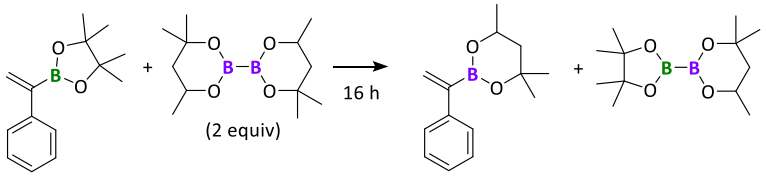
3.3.3. Influence of the solvent

We investigated the use of different solvents in the transborylation reaction to analyse the influence of polar and non-polar solvents in the reaction outcome. While substrate **3.9** was efficiently transborylated with B_2hex_2 in MeOH and EtOH, yielding product **3.20** in 86% and 80%, respectively, we conducted the reaction using several solvents (Table 3.2, entries 1 and 2).

The use of alternative solvents such as ^{i}PrOH proved to be less efficient for transborylation (Table 3.2, entry 3). To investigate whether the acidic properties of

the solvent could enhance the reaction outcome, we explored the use of polyfluorinated alcohols, specifically CF_3CH_2OH and $(CF_3)_2CHOH$ (HFIP). Although polyfluorinated alcohols possessed distinct physical and chemical properties that enabled unique reactivity modes,[30] the transborylated product **3.18** was only obtained in conversions between 12% and 16% (Table 3.2, entries 4 and 5). The use of THF as a solvent hindered the transborylation reaction (Table 3.2, entry 6). However, the addition of 2 equivalents of LiOMe to the reaction mixture in THF enabled the transborylation of **3.9** to **3.18**, although in lower yields in comparison to the use of MeOH as the solvent (Table 3.2, entry 7).

Table 3.2. Study of alternative solvents for the transborylation reaction.[a]



3.9 **3.18**

ENTRY	SOLVENT	YIELD[b] (%)
1	MeOH	86% [80%]
2	EtOH	80%
3	^{i}PrOH	9%
4	CF_3CH_2OH	12%
5	$(CF_3)_2CHOH$	16%
6	THF	0%
7	THF + LiOMe (2 equiv)	74% [42%]

[a]Reactions were performed with 0.3 mmol of model substrate **3.9** and 0.6 mmol of the diboron reagent in 2 mL of solvent. [b]Yields were calculated from the ^{1}H-NMR using naphthalene as an internal standard. Isolated yields in brackets.

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

Generalising the use of MeOH as the appropriate solvent, an *in-situ* NMR spectroscopy study on the evolution of the reactivity between **3.9** and 2 equivalents of B_2hex_2, in CD_3OD, was investigated. Figure 3.2 shows the evolution of the ^{1}H-NMR spectra along the reaction, illustrating that the new signals associated with the transborylated product **3.18** appeared after 3 h at 90 °C. Within 16 h the new alkenylborane **3.18** became the predominant species, as can be seen in the ^{1}H-NMR spectra (Figure 3.2).

On the other hand, a parallel *in-situ* ^{11}B-NMR spectroscopy study was conducted along the reaction (Figure 3.3). Remarkably, a 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 the formation of $R_2B–OCD_3$ species.

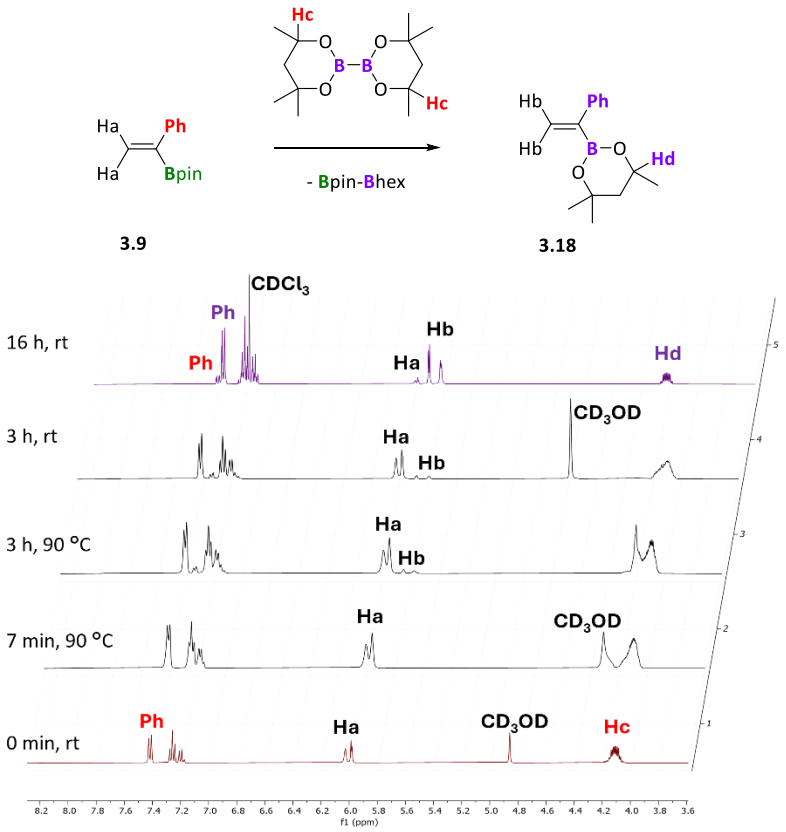


Figure 3.2. *In-situ* ^{1}H-NMR study for the reaction between 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**3.9**) and B_2hex_2.

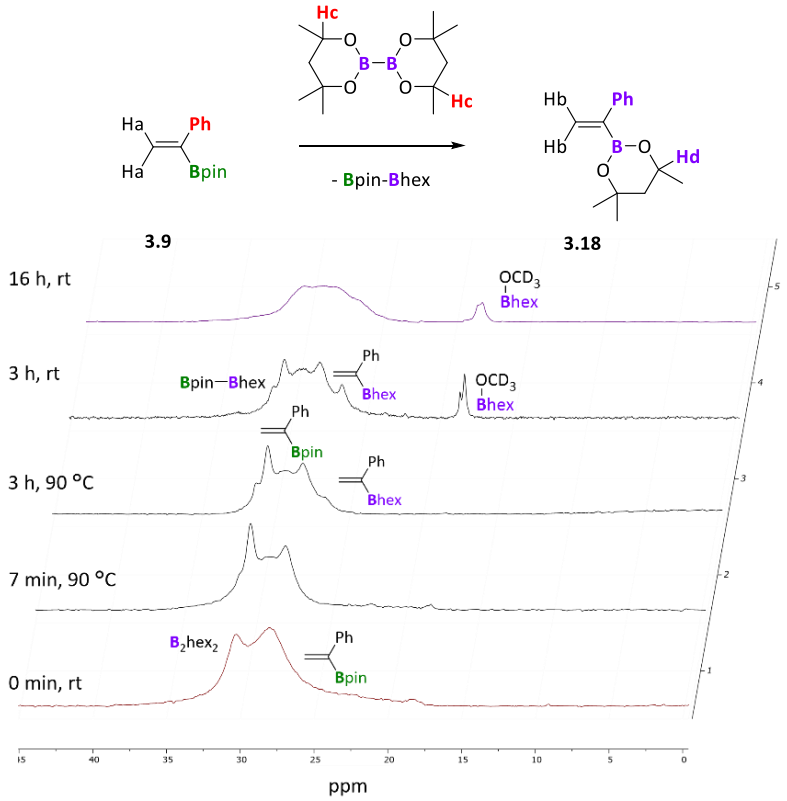
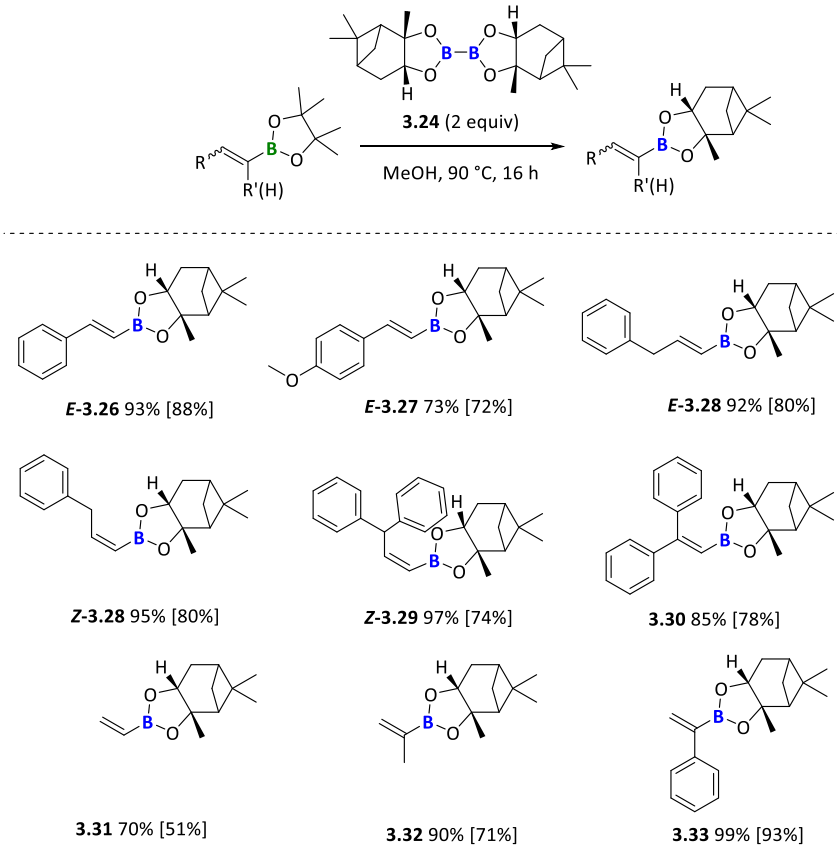


Figure 3.3. *In-situ* ^{11}B-NMR study for the reaction between 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (**3.9**) and B_2hex_2.

3.3.5. Transborylation reaction using chiral diboron reagents

The transborylation with chiral diboron reagents has been accomplished through representative 1,2-disubstituted alkenyl pinacolboronic esters and bis-(+)-pinanediolato diboron (B_2pai_2) (**3.24**) and (*S*,*S*)-B_2(O-CHPh-CHPh-O)$_2$ (**3.25**). Scheme 3.16 illustrates the scope of transborylated products with B_2pai_2. The relative (*E*)- or (*Z*)- configuration has been preserved from the substrates to the chiral alkenylboranes ***E*-3.28** and ***Z*-3.28**, providing the first synthetic approach for the (*Z*)-1,2-disubstituted alkenyl chiral boronic esters. Notably, these compounds cannot be synthesised using hydroboration protocols. The transborylation reaction of 1,1,2-trisubstituted substrate ***E*-3.6** allows the formation of chiral alkenyl boronic ester ***E*-3.30** with 78% isolated yield, demonstrating the compatibility of the methodology with sterically hindered substrates (Scheme 3.16). Similarly, substituted alkenyl (+)-

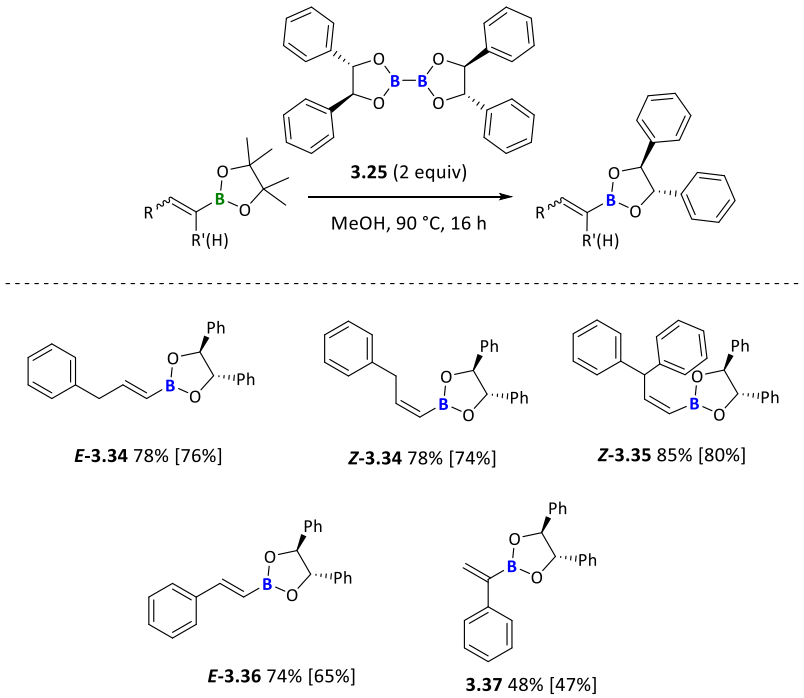
pinanediolboronic esters **3.31**-**3.33** were exclusively prepared through the transborylation reaction.



Scheme 3.16. Substrate scope for transborylation reaction of alkenyl pinacolboranes with chiral diboron reagent **3.24**. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

To extend the applicability for transborylation of vinylboranes employing chiral diboron reagents, we proved that (*S*,*S*)-B_2(O–CHPh–CHPh–O)$_2$ (**3.25**) effectively contributed to C(sp^2)–B/B'–B' cross-metathesis with 1,2-disubstituted vinyl boronic esters ***E*-3.1** and ***Z*-3.1**, yielding the corresponding alkenyl boronic esters ***E*-3.34** and ***Z*-3.34**, respectively (Scheme 3.17). The preservation of relative configuration throughout the transborylation process was a widely adopted strategy, demonstrated in the synthesis of chiral 1,2-disubstituted vinyl boronic esters ***Z*-3.35** and ***E*-3.36**. Additionally, the 1,1-disubstituted substrate **3.9** underwent transborylation with (*S*,*S*)-

$B_2(O–CHPh–CHPh–O)_2$ (**3.25**) yielding moderate yields, possibly due to the steric hindrance provided by the aryl groups present in the alkenylborane **3.37**.



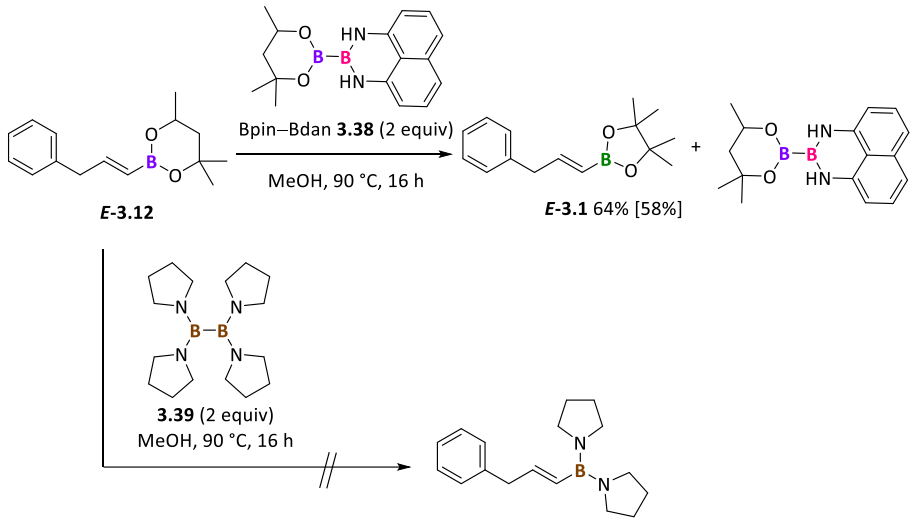
Scheme 3.17. Substrate scope for transborylation reaction of alkenyl pinacolboranes with chiral diboron reagent **3.25**. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

3.3.6. Chemoselective transborylation reaction

Taking into consideration the experimental findings about the transborylation of symmetrical diboron reagents to alkenyl pinacolboronic esters, we proceeded to examine the effect of unsymmetrical diboron reagent in the cross metathesis reaction.

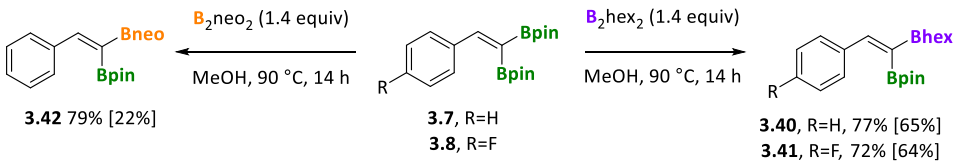
To study the chemoselectivity of the reaction, we conducted the transborylation of ***E*-3.12** with the mixed diboron reagent Bpin–Bdan (**3.38**) (dan = 1,8-diaminonaphthalene) and the tetraamino diboron reagent **3.39**. Interestingly, upon the addition of the mixed diboron reagent Bpin-Bdan to the alkenylborane ***E*-3.12** under optimised reaction conditions, the formation of a new $C(sp^2)$–B bond occurred with the most Lewis acidic boryl moiety, Bpin, resulting in the generation of alkenylborane ***E*-3.1** with an isolated yield of 58% (Scheme 3.18). As expected, this transborylation reaction failed to proceed in THF, even at 90 °C. Additionally,

alkenylborane ***E*-3.12** did not undergo transborylation with the tetramino diboron reagent **3.39**, under the optimised reaction conditions, indicating the difficulty to promote the cross-metathesis with this reagent that is characterised by lower Lewis acid properties (Scheme 3.18).



Scheme 3.18. Chemoselective transborylation reaction.

On the other hand, we investigated the transborylation of 1,1-diborylalkenes **3.7** and **3.8** with either B_2hex_2 or B_2neo_2 (1.4 equiv) in methanol at 90 °C, resulting in the formation of mixed 2-aryl 1,1-diborylalkenes **3.40**, **3.41** and **3.42** (Scheme 3.19). This transborylation process occurred stereoselectivity at the less sterically hindered position, as unambiguously demonstrated by one-dimensional Nuclear Overhauser Effect (1D NOE) experiments of compound **3.41** (Figure 3.4).



Scheme 3.19. Stereoselective transborylation reaction of 1,1-diborylalkenes. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

The aromatic protons of the aryl group (Hh and Hg) were assigned at 7.45 ppm and 6.97 ppm, respectively, as well as the olefinic proton (Ha) that can be observed at 7.61 ppm. The protons of the Bhex moiety (Hb, Hc, Hc, He, and Hf) can be observed at 4.24

ppm, 1.76 ppm, 1.53 ppm, 1.30 ppm, and 1.26 ppm, respectively. Finally, the protons of the Bpin moiety (Hd) can be observed at 1.31 ppm.

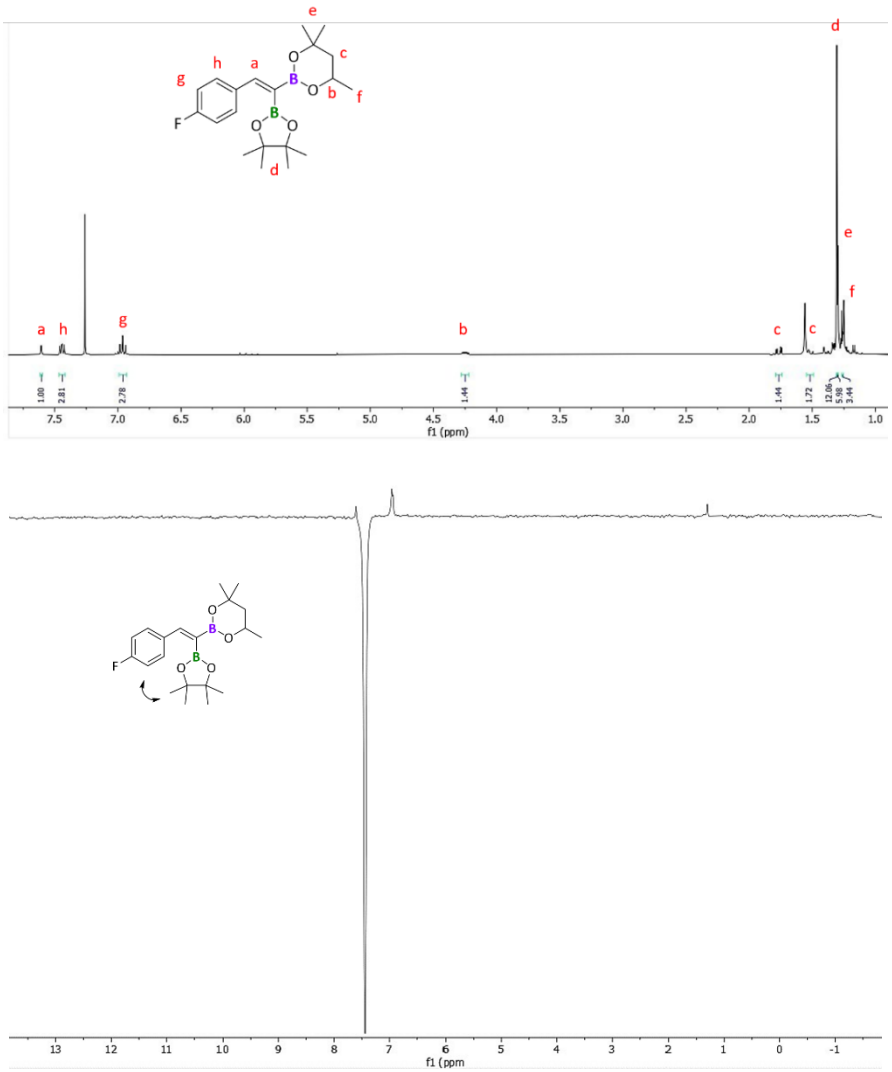


Figure 3.4. For comparison, ^{1}H-NMR study and 1D NOE experiment irradiating at 7.45 ppm of product **3.41**.

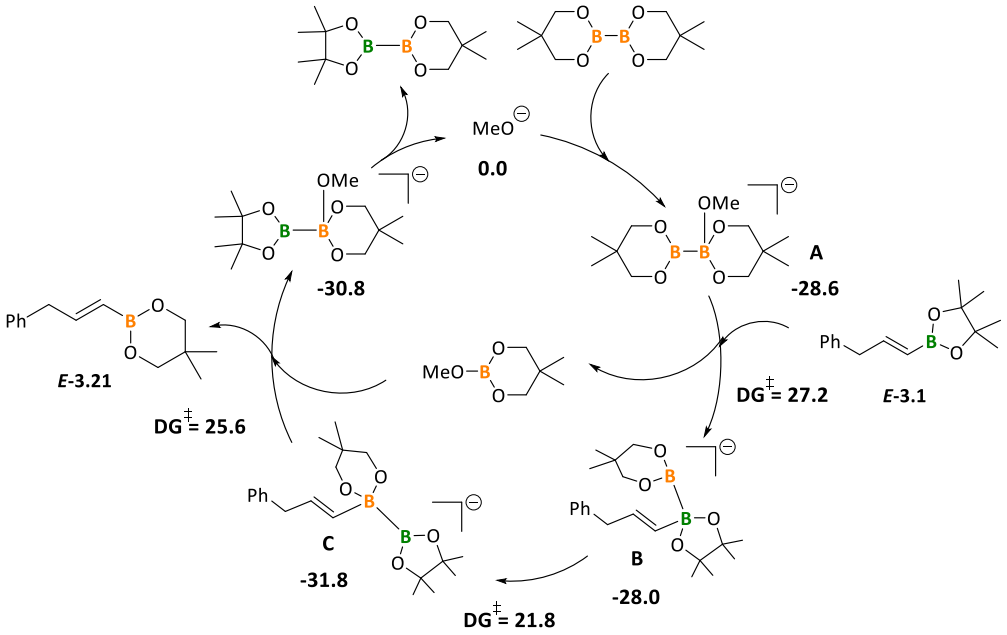
To conduct the 1D NOE experiment of product **3.41**, the aryl protons were selected to be irradiated to justify the stereoselectivity. The irradiated protons at 7.45 ppm disclosed two main signals in the experiment corresponding to the aryl protons (Hg = 6.97 ppm), the olefinic proton (Ha = 7.61 ppm) and the Bpin (Hd = 1.31 ppm). This fact was in accordance with the assignment of the proposed stereoisomer.

3.4. Computational studies (carried out by Prof. Carbó)

To study the mechanism for the C(sp^2)–Bpin/B–B transborylation reaction, in collaboration with Gerard Bru, Ricardo J. Maza, and Prof. Jorge J. Carbó, DFT calculations were performed with model symmetric diboron reagent (Scheme 3.20).[31]

The role of the alcohol used as solvent or the alkoxy base in transborylation was associated with the activation of the diboron reagent. In the case of methanol, methoxide could be generated through autoprotolysis, and the mechanism proposed by DFT calculations could be divided into four steps. The first step was the coordination of the methoxide to the B–B bond inducing nucleophilic character to Bneo(sp^2) moiety,[32] followed by the nucleophilic attack of the activated diboron **A** to the electrophilic C(sp^2) –B bond of the substrate ***E*-3.1**, leading to the formation of MeOBneo and the intermediate **B** where the Bpin moiety was quaternised. The next step consisted of shifting the alkenyl fragment from the Bpin to the Bneo moiety resulting in structure **C**, in which the Bneo was now quaternised. Finally, the $MeO^{-}\rightarrow$ Bneo-Bpin adduct and the transborylated alkene ***E*-3.21** were formed by interaction of the Bpin moiety of intermediate **C** with the electrophilic boron of MeOBneo.

The suggested mechanism preserved the stereochemistry of the original alkene in agreement with the experimental evidence. Furthermore, the reaction was calculated to be modestly exergonic, with an energy release of -0.8 $kcal \cdot mol^{-1}$. However, the use of an excess of the diboron reagent (2 equiv) might provide additional driving force for the reaction.



Scheme 3.20. Suggested mechanism for the transborylation of ***E*-3.1** with B_2neo_2 in the presence of MeOH. Relative free energies and barriers in kcal·mol^{-1}. DFT calculations performed by G. Bru, R. J. Maza and J. J. Carbó. Picture adapted by the calculated energetic profile.

3.5. Conclusions

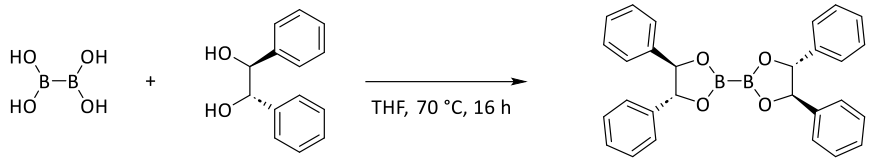
Our studies led to the development of the first C(sp^2)–B/B'–B' cross-metathesis reaction. We conclude that the stereospecific exchange of boryl moieties between alkenylboranes and diboron reagents has been demonstrated for (*E*)-1,2-, (*Z*)-1,2-, 1,1-, and 1,1,2-substituted alkenylboranes, with the respective formation of mixed diboranes. This represents a fundamentally different approach to the synthesis of alkenylboranes.

An attractive and distinctive feature of this method is the access to the synthesis of chiral alkenylboranes from simple starting materials that can transborylate with chiral diboron reagents. Spectroscopic and theoretical studies have provided significant insights to the mechanism of the transborylation reaction.

3.6. Experimental section

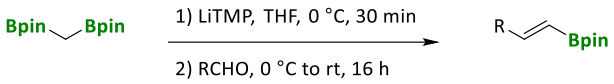
General information. All solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures.[33] Diboron reagents were purchased from Dalian Allychem Co. and were used without further purification. All air-sensitive reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon using Schlenk-type techniques. Flash chromatography purification procedures were performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Analytical Thin Layer Chromatography (TLC) was performed on Merck Kieselgel 60 F254 and was developed using standard visualising agents: UV fluorescence (254 and 366 nm) or potassium permanganate. NMR spectra were recorded at a Varian 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm ^{1}H and 77.16 ppm ^{13}C). ^{11}B NMR chemical shifts (δ) are reported in ppm relative to $BF_3{\cdot}Et_2O$. Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sp = septet, m = multiplet. Melting points were measured using open glass capillaries in a Digital Melting Point IA 9100 apparatus. High-Resolution Mass Spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies with an ESI interface that is located at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona), or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or EI interface that is located at the Unidade de Espectrometría de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela). GC-MS analyses were performed on an 8860 GC System with a 5977B GC/MSD from Agilent Technologies equipped with a capillary column HP-5MS Ultra Inert (30 m, 0.25 mm i.d., 0.25 µm thickness) and using He as the carrier gas.

Synthesis of chiral diboron compound (3.25)



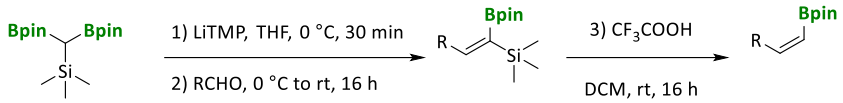
This procedure was adapted from a previous methodology described by W. Tang et al.[34] An oven-dried Schlenk flask, equipped with a magnetic stir bar, was charged with activated molecular sieves (4 Å), tetrahydroxy diboron (1 mmol, 1 equiv) and (S,S)-(−)-hydrobenzoin (2 mmol, 2 equiv) in THF (2 mL). The reaction mixture was stirred at 70 °C, for 16 h, and the crude mixture was filtered through a pad of Celite. The solvents were removed under vacuum to obtain a white solid that was crystallised in ethyl acetate. The white solid was filtered and washed with cold ethyl acetate to obtain the product **3.25** (54%, 240 mg).

Synthesis of (*E*)-alkenyl pinacolboranes



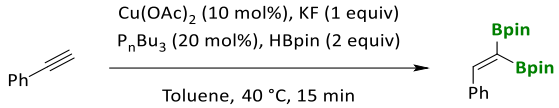
A Schlenk-tube, equipped with a magnetic stir bar, was charged with bis(pinacolboryl)methane (0.5 mmol, 1 equiv) and LiTMP (0.6 mmol, 1.2 equiv) in dry THF as solvent (2 mL). The mixture was stirred for 30 min at 0 °C. Then, the aldehyde (0.8 mmol, 1.6 equiv) was added. The reaction was stirred for 10 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 by comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

Synthesis of (*Z*)-alkenyl pinacolboranes



A Schlenk-tube, equipped with a magnetic stir bar, was charged with $HC(SiMe_3)(Bpin)_2$ (0.5 mmol, 1 equiv) and LiTMP (0.6 mmol, 1.2 equiv) in dry THF as solvent (2 mL). The mixture was stirred for 30 min at 0 °C. Then, the aldehyde (0.8 mmol, 1.6 equiv) was added. The reaction was stirred for 10 min at 0 °C, followed by 16 h at room temperature. The solvent was gently concentrated at the Schlenk line. Next, a solution of 3 mL of dichloromethane containing CF_3COOH (3 mmol, 8 equiv) was 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 by comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

Synthesis of 1,1-diborylalkenes: example of 2,2'-(2-phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

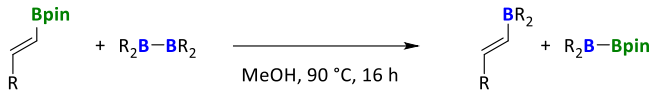


3.7 [58%]

A Schlenk-tube, equipped with a magnetic stir bar, was charged with $Cu(OAc)_2$ (10 mol%, 36 mg), KF (116 mg, 2 mmol, 1 equiv) in dry toluene as solvent (2.5 mL). Then, P_nBu_3 (20 mol%, 99 µL), ethynylbenzene (0.22 mL, 2 mmol), and HBpin (0.58 mL, 4 mmol, 2 equiv) were added in this order. The mixture was stirred for 15 min at 40 °C. The reaction mixture was then diluted with Et_2O and filtered through a plug of celite in the air with copious washing (Et_2O). 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. Isolated yield for **3.7**: [58%].

Transborylation of alkenylboranes with diboron reagents

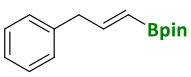
General procedure for transborylation of alkenylboranes with diboron reagents



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

- Characterisation data for alkenyl pinacolboranes

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*E*-3.1)[35]



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (61%, 75 mg).

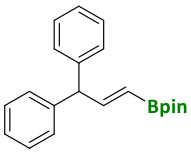
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 – 7.13 (m, 2H), 7.15 – 7.04 (m, 3H), 6.68 (dt, J = 17.8, 6.3 Hz, 1H), 5.37 (dt, J = 17.8, 1.7 Hz, 1H), 3.39 (dd, J = 6.3, 1.7 Hz, 2H), 1.16 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 139.1, 128.9, 128.4, 126.1, 83.1, 42.3, 24.8.

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

HRMS (ESI) for **$C_{15}H_{25}NBO_2$ $[M+NH_4^+]^+$:** calculated: 262.1979, found: 262.1978.

(*E*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*E*-3.2)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (94%, 151 mg).

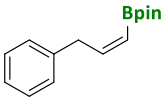
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.25 (m, 5H), 7.23 – 7.16 (m, 5H), 7.05 (dd, J = 17.9, 6.9 Hz, 1H), 5.40 (dd, J = 17.9, 1.5 Hz, 1H), 4.80 (dd, J = 6.9, 1.5 Hz, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 142.6, 130.0, 128.8, 128.4, 126.4, 83.2, 56.8, 24.8.

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

HRMS (ESI) for **$C_{21}H_{29}NBO_2$ $[M+NH_4^+]^+$:** calculated: 338.2291, found: 338.2299.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*Z*-3.1)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (36%, 44 mg).

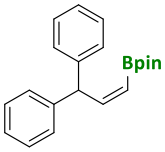
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.25 (m, 2H), 7.26 – 7.13 (m, 3H), 6.55 (dt, J = 14.3, 7.5 Hz, 1H), 5.43 (dt, J = 13.3, 1.4 Hz, 1H), 3.76 (dt, J = 7.6, 0.9 Hz, 2H), 1.30 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.6, 140.6, 128.6, 128.4, 125.9, 83.0, 38.6, 24.8.

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

HRMS (ESI) for **$C_{15}H_{25}NBO_2$ $[M+NH_4^+]^+$:** 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*-3.2)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (71%, 114 mg).

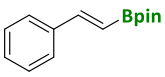
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 – 7.25 (m, 5H), 7.25 – 7.17 (m, 5H), 6.85 (dd, J = 13.2, 10.4 Hz, 1H), 5.65 (dd, J = 10.3, 0.6 Hz, 1H), 5.52 (dd, J = 13.2, 0.6 Hz, 1H), 1.28 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 144.2, 128.4, 128.3, 126.1, 83.1, 51.9, 30.9, 24.9.

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

HRMS (ESI) for **$C_{21}H_{29}NBO_2$ $[M+NH_4^+]^+$:** calculated: 338.2302, found: 338.2291.

(*E*)-4,4,5,5-Tetramethyl-2-(2-phenylethenyl)-1,3,2-dioxaborolane (*E*-3.3)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (68%, 79 mg).

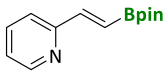
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.45 (m, 2H), 7.40 (d, J = 18.5 Hz, 1H), 7.38 – 7.26 (m, 3H), 6.17 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.5, 128.9, 128.5, 127.0, 83.3, 24.8.

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

HRMS (ESI) for **$C_{14}H_{20}BO_2$ [M+H$^+$]$^+$:** calculated: 231.1556, found: 231.1555.

(*E*)-2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (*E*-3.4)[26]



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (40%, 47 mg).

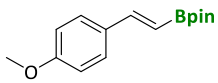
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (dd, J = 4.8, 1.8 Hz, 1H), 7.65 (dt, J = 7.7, 1.8 Hz, 1H), 7.45 (d, J = 18.3 Hz, 1H), 7.40 (dt, J = 7.9, 1.1 Hz, 1H), 7.17 (dd, J = 7.5, 4.8 Hz, 1H), 6.63 (d, J = 18.3 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.4, 149.7, 148.7, 136.4, 123.0, 122.2, 83.4, 24.8.

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

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

(*E*)-4,4,5,5-Tetramethyl-2-(4-methoxystyryl)-1,3,2-dioxaborolane (*E*-3.5)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (73%, 95 mg).

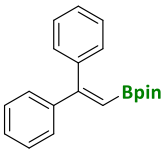
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.34 (m, 2H), 7.28 (d, J = 18.4 Hz, 1H), 6.83 – 6.77 (m, 2H), 5.94 (d, J = 18.4 Hz, 1H), 3.75 (s, 3H), 1.24 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 149.0, 130.4, 128.4, 113.9, 113.3, 83.2, 55.3, 24.8.

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

HRMS (ESI) for **$C_{15}H_{22}BO_3$ [M+H$^+$]$^+$:** calculated: 261.1662, found: 261.1667.

2-(2,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*-3.6)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (61%, 94 mg).

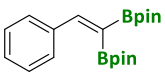
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.24 (m, 10H), 5.99 (s, 1H), 1.15 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 129.8, 128.2, 128.0, 127.9, 127.6, 127.5, 83.1, 24.6.

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

HRMS (ESI) for **$C_{20}H_{24}BO_2$ [M+H$^+$]$^+$:** calculated: 307.1869, found: 307.1877.

2,2'-(2-Phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3.7)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (58%, 68 mg).

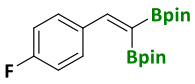
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (s, 1H), 7.51 – 7.44 (m, 2H), 7.34 – 7.27 (m, 3H), 1.31 (s, 12H), 1.28 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 139.6, 128.4, 128.1, 128.1, 83.6, 83.2, 24.8, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.84.

HRMS (ESI) for **$C_{20}H_{30}B_2O_4$ [M+H$^+$]$^+$:** calculated: 371.2568, found: 371.2567.

2,2'-(2-(4-Fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3.8)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (44%, 56 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.49 – 7.43 (m, 2H), 6.98 (t, J = 8.7 Hz, 2H), 1.31 (s, 12H), 1.27 (s, 12H).

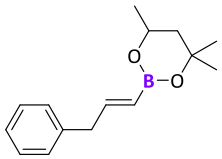
^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 129.9, 129.8, 115.2, 114.9, 83.6, 83.2, 24.8, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.86.

HRMS (ESI) for **$C_{20}H_{29}B_2FO_4$ [M+H$^+$]$^+$:** calculated: 375.2210, found: 375.2215.

- Characterisation data for transborylated alkenylboranes

(*E*)-4,4,6-Trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (*E*-3.12)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (89%, 65 mg).

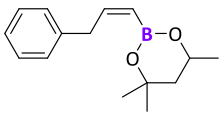
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 – 7.17 (m, 2H), 7.11 (dt, J = 6.4, 1.2 Hz, 3H), 6.57 (dt, J = 17.6, 6.4 Hz, 1H), 5.30 (d, J = 17.6 Hz, 1H), 4.18 – 4.05 (m, 1H), 3.37 (d, J = 6.4 Hz, 2H), 1.69 (dd, J = 13.9, 3.0 Hz, 1H), 1.41 (dd, J = 13.9, 11.6 Hz, 1H), 1.20 (s, 6H), 1.17 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.0, 139.7, 128.9, 128.4, 126.0, 70.6, 64.6, 45.9, 42.0, 31.2, 28.1, 23.1.

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

HRMS (ESI) for **$C_{15}H_{25}NBO_2$ [M+NH$_4^+$]$^+$:** calculated: 262.1978, found: 262.1988.

(*Z*)-4,4,6-Trimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (*Z*-3.12)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (69%, 51 mg).

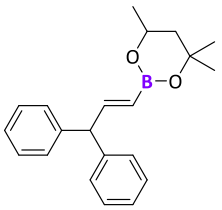
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.15 (m, 4H), 7.15 – 7.07 (m, 1H), 6.33 (dt, J = 13.5, 7.6 Hz, 1H), 5.25 (d, J = 13.5 Hz, 1H), 4.20 (m, 1H), 3.68 (d, J = 7.6, 2H), 1.74 (dd, J = 13.9, 2.9 Hz, 1H), 1.53 – 1.42 (m, 1H), 1.26 (d, 6H), 1.22 (d, J = 2.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 141.3, 128.6, 128.3, 125.7, 70.8, 64.7, 45.9, 37.9, 31.3, 28.2, 24.8, 23.2.

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

HRMS (ESI) for **$C_{15}H_{25}NBO_2$ [M+NH_4^+]$^+$:** calculated: 262.1978, found: 262.1988.

(*E*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*E*-3.13)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (77%, 74 mg).

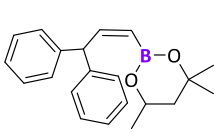
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 – 7.29 (m, 4H), 7.25 (m, 6H), 7.01 (dd, J = 17.6, 6.8 Hz, 1H), 5.37 (dd, J = 17.7, 1.5 Hz, 1H), 4.83 (dd, J = 6.9, 1.5 Hz, 1H), 4.26 (m, 1H), 1.82 (dd, J = 13.9, 2.9 Hz, 1H), 1.66 – 1.48 (m, 1H), 1.34 (s, 6H), 1.20 (d, J = 2.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 143.1, 132.4, 130.0, 128.8, 128.3, 128.3, 126.2, 70.7, 64.6, 56.6, 45.9, 31.2, 28.1.

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

HRMS (ESI) for **$C_{21}H_{26}BO_2$ [M+H^+]$^+$:** calculated: 320.7415, found: 320.7442.

(*S*,*Z*)-2-(3,3-Diphenylprop-1-en-1-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*Z*-3.13)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (32%, 31 mg).

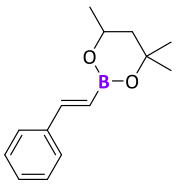
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 – 7.27 (m, 5H), 7.27 – 7.16 (m, 4H), 6.74 (dd, J = 13.4, 10.2 Hz, 1H), 5.76 (d, J = 10.2 Hz, 1H), 5.44 (d, J = 13.4 Hz, 1H), 4.27 (m, 1H), 1.81 (dd, J = 13.9, 2.9 Hz, 1H), 1.57 – 1.48 (m, 1H), 1.34 (s, 3H), 1.31 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.2, 128.3, 125.9, 70.9, 64.8, 51.1, 45.8, 31.3, 30.9, 28.2, 23.2.

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

HRMS (ESI) for **$C_{21}H_{29}NBO_2$ [M+NH_4^+]$^+$:** calculated: 338.2302, found: 338.2291.

(*E*)-4,4,6-Trimethyl-2-(2-phenylethenyl)-1,3,2-dioxaborinane (*E*-3.14)[29]



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (62%, 43 mg).

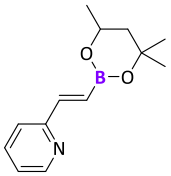
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 – 7.43 (m, 2H), 7.33 – 7.20 (m, 4H), 6.09 (d, J = 18.2 Hz, 1H), 4.26 (m, 1H), 1.80 (dd, J = 13.9, 2.9 Hz, 1H), 1.54 (dd, J = 12.7, 12.6 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H).

^{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.

HRMS (ESI) for **$C_{14}H_{20}BO_2$ [M+H^+]$^+$:** calculated: 231.1556, found: 231.1569.

(*E*)-2-(2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)pyridine (*E*-3.15)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (56%, 39 mg).

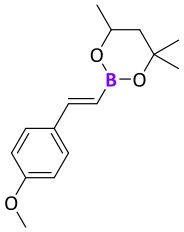
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (dd, J = 4.8, 1.8 Hz, 1H), 7.63 (t, J = 7.7, 1.9 Hz, 1H), 7.47 (dd, J = 8.0, 1.1 Hz, 1H), 7.39 (d, J = 18.2 Hz, 1H), 7.13 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 6.48 (d, J = 18.2 Hz, 1H), 4.28 (m, 1H), 1.82 (dd, J = 13.9, 3.0 Hz, 1H), 1.55 (dd, J = 13.9, 11.6 Hz, 1H), 1.33 (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 **$C_{13}H_{19}NBO_2$ [M+H$^+$]$^+$:** calculated: 230.1467, found: 230.1474.

(*E*)-2-(4-Methoxystyryl)-4,4,6-trimethyl-1,3,2-dioxaborinane (*E*-3.16)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (80%, 62 mg).

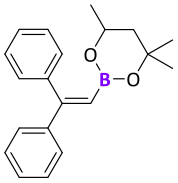
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.38 (m, 2H), 7.31 – 7.21 (d, J = 18.2 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.95 (d, J = 18.2 Hz, 1H), 4.27 (m, 1H), 3.81 (s, 3H), 1.82 (dd, J = 13.9, 2.9 Hz, 1H), 1.60 – 1.49 (m, 2H), 1.34 (s, 3H), 1.33 (s, 3H), 1.31 (d, J = 6.2 Hz, 3H).

^{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 **$C_{15}H_{22}BO_3$ [M+H$^+$]$^+$:** calculated: 261.1662, found: 261.1658.

2-(2,2-Diphenylvinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (3.17)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (92%, 84 mg).

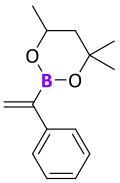
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 – 7.20 (m, 10H), 6.00 (s, 1H), 4.09 (m, 1H), 1.69 (dd, J = 13.9, 3.0 Hz, 1H), 1.47 – 1.33 (m, 1H), 1.17 (s, 3H), 1.08 (s, 4H), 1.06 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.10, 143.37, 142.60, 129.72, 127.88, 127.84, 127.61, 127.43, 127.05, 70.87, 64.83, 45.77, 30.89, 27.80, 22.89.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.14.

HRMS (ESI) for **$C_{20}H_{27}NBO_2$ [M+NH_4^+]$^+$:** calculated: 472.2830, found: 472.2834.

4,4,6-Trimethyl-2-(1-phenylvinyl)-1,3,2-dioxaborinane (3.18)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (80%, 55 mg).

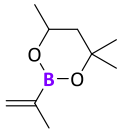
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.40 (m, 2H), 7.35 – 7.25 (m, 2H), 7.26 – 7.17 (m, 1H), 5.98 (d, J = 3.5 Hz, 1H), 5.90 (d, J = 3.5 Hz, 1H), 4.29 (m, 1H), 1.84 (dd, J = 13.9, 3.0 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.33 (s, 6H), 1.30 (d, J = 6.2 Hz, 3H).

^{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 **$C_{14}H_{23}NBO_2$ [M+NH_4^+]$^+$:** calculated: 248.1822, found: 248.1831.

4,4,6-Trimethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborinane (3.19)



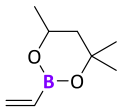
The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (15%, 8 mg).

^{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.

4,4,6-Trimethyl-2-vinyl-1,3,2-dioxaborinane (3.20)



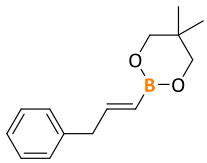
The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (30%, 14 mg).

^{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.

(*E*)-5,5-Dimethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborinane (*E*-3.21)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (48%, 33 mg).

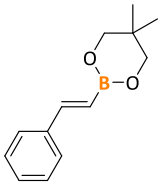
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.25 (m, 2H), 7.19 (t, J = 7.5 Hz, 3H), 6.67 (dt, J = 17.6, 6.4 Hz, 1H), 5.39 (dt, J = 17.6, 1.6 Hz, 1H), 3.62 (s, 4H), 3.46 (dd, J = 6.5, 1.6 Hz, 2H), 0.96 (s, 6H).

^{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 **$C_{14}H_{23}NBO_2$ $[M+NH_4^+]^+$:** calculated: 262.1978, found: 262.1978.

(*E*)-5,5-Dimethyl-2-(2-phenylethenyl)-1,3,2-dioxaborinane (*E*-3.22)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (68%, 44 mg).

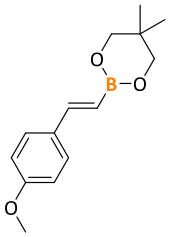
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 – 7.46 (m, 2H), 7.38 – 7.23 (m, 4H), 6.11 (d, J = 18.3 Hz, 1H), 3.70 (s, 4H), 1.01 (s, 6H).

^{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.

HRMS (ESI) for **$C_{26}H_{35}B_2O_4$ $[2M+H^+]^+$:** calculated: 432.2817, found: 432.2643.

(*E*)-2-(4-Methoxystyryl)-5,5-dimethyl-1,3,2-dioxaborinane (*E*-3.23)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (64%, 47 mg).

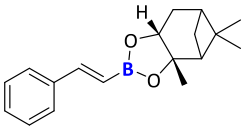
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 – 7.39 (m, 2H), 7.28 (d, J = 17.3 Hz, 1H), 6.92 – 6.80 (m, 2H), 5.95 (d, J = 18.2 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 4H), 0.98 (s, 6H).

^{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 **$C_{14}H_{20}BO_3$ $[M+H]^+$:** calculated: 247.1506, found: 247.1507.

(3a*R*,4*S*,6*S*,7a*R*)-3a,5,5-Trimethyl-2-((*E*)-styryl)hexahydro-4,6-methanobenzo[*d*][1,3,2] dioxaborole (*E*-3.26)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (88%, 74 mg).

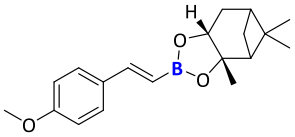
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 – 7.46 (m, 2H), 7.41 (d, J = 18.5 Hz, 1H), 7.39 – 7.25 (m, 3H), 6.20 (d, J = 18.4 Hz, 1H), 4.38 (dd, J = 8.7, 1.9 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.30 – 2.19 (m, 1H), 2.12 (t, J = 6.0, 4.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.21 (d, J = 10.9 Hz,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

^{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 **$C_{36}H_{46}B_2O_4$ [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 (*E*-3.27)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (72%, 68 mg).

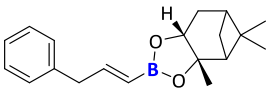
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.40 (m, 2H), 7.36 (d, J = 18.4 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.03 (d, J = 18.4 Hz, 1H), 4.36 (dd, J = 8.7, 1.9 Hz, 1H), 3.82 (s, 3H), 2.39 (m, 1H), 2.30 – 2.17 (m, 1H), 2.11 (dd, J = 6.1, 4.9 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.45 (s, 3H), 1.31 (s, 3H), 1.26 – 1.16 (m, 1H), 0.87 (s, 3H).

^{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.

HRMS (ESI) for **$C_{19}H_{26}BO_3$ [M+H$^+$]$^+$:** calculated: 313.1975, found: 313.1987.

(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 (*E*-3.28)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (80%, 71 mg).

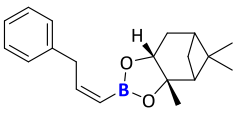
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.31 (m, 2H), 7.31 – 7.22 (m, 3H), 6.84 (dt, J = 17.8, 6.4 Hz, 1H), 5.55 (dt, J = 17.8, 1.6 Hz, 1H), 4.36 (dd, J = 8.7, 1.9 Hz, 1H), 3.56 (m, 2H), 2.41 (ddt, J = 14.0, 8.7, 2.2 Hz, 1H), 2.35 – 2.22 (m, 1H), 2.12 (dd, J = 6.1, 4.9 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.22 (d, J = 10.9 Hz, 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 **$C_{19}H_{29}NBO_2$ [M+NH_4^+]$^+$:** calculated: 314.2291, found: 314.2302.

(3a*S*,7a*R*)-3a,5,5-trimethyl-2-((*Z*)-3-phenylprop-1-en-1-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (*Z*-3.28)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (80%, 71 mg).

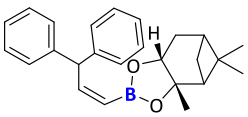
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.24 (m, 3H), 7.24 – 7.15 (m, 3H), 6.57 (dt, J = 13.3, 7.6 Hz, 1H), 5.47 (dt, J = 13.3, 1.4 Hz, 1H), 4.35 (dd, J = 8.7, 1.8 Hz, 1H), 3.84 – 3.70 (m, 2H), 2.44 – 2.31 (m, 1H), 2.30 – 2.19 (m, 1H), 2.10 (dd, J = 6.1, 4.8 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.31 (s, 3H), 1.25 – 1.18 (m, 1H), 0.87 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.60, 140.64, 128.64, 128.43, 125.92, 85.43, 77.58, 51.40, 39.61, 38.70, 38.14, 35.62, 28.72, 27.11, 26.53, 24.03.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.48.

HRMS (ESI) for **$C_{19}H_{29}NBO_2$ [M+NH_4^+]$^+$:** calculated: 314.2291, found: 314.2294.

(3a*S*,7a*R*)-2-((*Z*)-3,3-Diphenylprop-1-en-1-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (*Z*-3.29)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (74%, 83 mg).

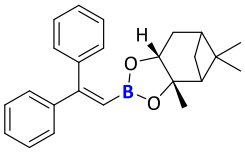
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13 – 7.06 (m, 4H), 7.06 – 6.96 (m, 6H), 6.67 (dd, *J* = 13.2, 10.3 Hz, 1H), 5.45 (d, *J* = 10.3 Hz, 1H), 5.36 (d, *J* = 13.2 Hz, 1H), 4.14 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.06 – 1.95 (m, 1H), 1.90 (dd, *J* = 6.1, 4.9 Hz, 1H), 1.76 – 1.65 (m, 2H), 1.23 (s, 3H), 1.11 (s, 3H), 0.95 (d, *J* = 10.9 Hz, 1H), 0.67 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.09, 144.26, 144.20, 128.44, 128.41, 126.17, 85.53, 77.63, 52.10, 51.39, 39.60, 38.14, 35.60, 28.69, 27.12, 26.50, 24.91, 24.04.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 28.79.

HRMS (ESI) for **$C_{25}H_{30}BO_2$ [M+H$^+$]$^+$:** calculated: 373.3210, found: 373.3204.

(3a*S*,4*S*,6*S*,7a*R*)-2-(2,2-Diphenylvinyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[*d*][1,3,2]dioxaborole (3.30)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (78%, 84 mg).

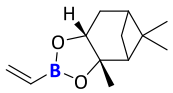
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.20 (m, 10H), 6.01 (s, 1H), 4.15 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.24 – 2.09 (m, 2H), 1.95 (t, *J* = 5.5 Hz, 1H), 1.83 (tt, J = 5.9, 3.1 Hz, 1H), 1.63 (ddd, *J* = 14.5, 3.4, 2.1 Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H), 1.10 (d, *J* = 10.7 Hz, 1H), 0.77 (s, 3H).

^{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 **$C_{24}H_{28}BO_2$ [M+H$^+$]$^+$:** calculated: 359.2191, found: 359.2182.

(3aS,7aR)-3a,5,5-Trimethyl-2-vinylhexahydro-4,6 methanobenzo[d][1,3,2]dioxaborole (3.31)



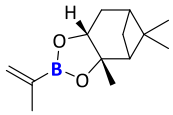
The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (51%, 32 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.16 (dd, *J* = 19.4, 4.2 Hz, 1H), 6.03 (dd, *J* = 13.6, 4.3 Hz, 1H), 5.89 (dd, *J* = 19.4, 13.7 Hz, 1H), 4.32 (dd, *J* = 8.8, 1.9 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.28 – 2.16 (m, 1H), 2.10 – 2.03 (m, 1H), 1.95 – 1.85 (m, 2H), 1.41 (s, 3H), 1.29 (s, 3H), 1.15 (d, *J* = 11.0 Hz, 1H), 0.85 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.13, 85.92, 77.95, 53.56, 51.48, 39.66, 38.31, 35.60, 28.75, 27.24, 26.56, 24.16.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.35.

(3aS,7aR)-3a,5,5-Trimethyl-2-(prop-1-en-2-yl)hexahydro-4,6-methanobenzo[d] [1,3,2]dioxaborole (3.32)



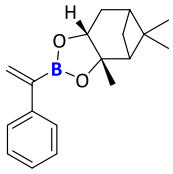
The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (71%, 47 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.78 – 5.72 (m, 1H), 5.67 – 5.60 (m, 1H), 4.32 (dd, *J* = 8.7, 1.9 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.27 – 2.16 (m, 1H), 2.11 – 2.03 (m, 1H), 1.94 – 1.85 (m, 2H), 1.84 (t, *J* = 1.5 Hz, 3H), 1.41 (s, 2H), 1.29 (s, 2H), 0.85 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 130.08, 86.03, 78.13, 51.50, 39.66, 38.30, 35.70, 28.81, 27.24, 26.59, 24.94, 24.16, 21.44.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.52.

(3aS,7aR)-3a,5,5-Trimethyl-2-(1-phenylvinyl)hexahydro-4,6-methanobenzo[d] [1,3,2]dioxaborole (3.33)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (93%, 79 mg).

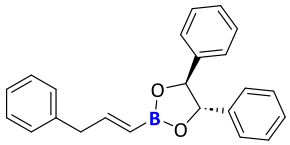
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 – 7.45 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 6.08 (d, *J* = 2.0 Hz, 2H), 4.41 (dd, *J* = 8.8, 1.9 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.32 – 2.21 (m, 1H), 2.16 – 2.09 (m, 1H), 2.01 – 1.90 (m, 2H), 1.46 (s, 3H), 1.31 (s, 3H), 1.25 (d, *J* = 10.9 Hz, 1H), 0.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.67, 131.11, 128.33, 127.32, 127.16, 86.34, 78.38, 51.52, 39.69, 38.32, 35.70, 28.83, 27.25, 26.74, 24.18.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.04.

HRMS (ESI) for **$C_{18}H_{24}BO_2$ [M+H$^+$]$^+$:** calculated: 283.1869, found: 283.1854.

(4*R*,5*R*)-4,5-Diphenyl-2-((*E*)-3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*E*-3.34)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (76%, 78 mg).

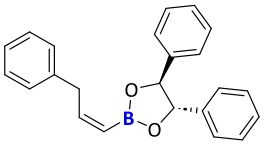
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 – 7.23 (m, 12H), 7.24 – 7.14 (m, 3H), 6.96 (dtd, *J* = 17.9, 6.5, 1.3 Hz, 1H), 5.63 (dq, *J* = 17.8, 1.6 Hz, 1H), 5.13 (s, 2H), 3.54 (dd, *J* = 6.4, 1.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.15, 140.32, 138.93, 128.92, 128.77, 128.55, 128.32, 126.30, 125.85, 86.42, 42.40.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.37.

HRMS (ESI) for **$C_{23}H_{25}NBO_2$ [M+NH$_4^+$]$^+$:** calculated: 358.1978, found: 358.1997.

(4R,5R)-4,5-Diphenyl-2-((Z)-3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (*Z*-3.34)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (74%, 76 mg).

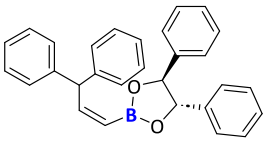
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.24 (m, 15H), 7.24 – 7.17 (m, 1H), 6.76 (dt, *J* = 13.3, 7.6 Hz, 1H), 5.67 (dt, *J* = 13.3, 1.4 Hz, 1H), 5.24 (s, 2H), 3.89 (dd, *J* = 7.6, 1.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.54, 140.43, 140.32, 128.80, 128.65, 128.50, 128.33, 126.05, 125.80, 86.28, 38.89.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.84.

HRMS (ESI) for **$C_{23}H_{25}NBO_2$ [M+NH_4^+]$^+$:** calculated: 358.1978, found: 358.1955.

(4*R*,5*R*)-2-((*Z*)-3,3-Diphenylprop-1-en-1-yl)-4,5-diphenyl-1,3,2-dioxaborolane (*Z*-3.35)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (80%, 101 mg).

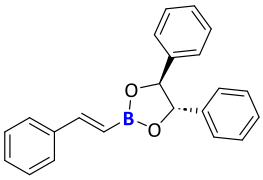
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 – 7.13 (m, 21H), 7.03 (dd, *J* = 13.3, 10.4 Hz, 1H), 5.78 – 5.70 (m, 2H), 5.18 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.56, 196.78, 156.97, 144.10, 144.05, 132.45, 130.11, 129.71, 128.82, 128.56, 128.54, 128.52, 128.42, 128.35, 128.32, 128.04, 126.35, 125.81, 86.37, 52.43.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.08.

HRMS (ESI) for **$C_{29}H_{25}BO_2Na$ [M+Na^+]$^+$:** calculated: 439.1845, found: 439.1853.

(4*R*,5*R*)-4,5-Diphenyl-2-((*E*)-styryl)-1,3,2-dioxaborolane (*E*-3.36)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (65%, 64 mg).

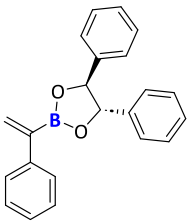
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, *J* = 18.5 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.44 – 7.32 (m, 13H), 6.37 (d, *J* = 18.4 Hz, 1H), 5.26 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.07, 149.53, 140.32, 137.32, 129.25, 128.83, 128.69, 128.40, 127.26, 125.87, 86.59, 83.37, 65.87.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.55.

HRMS (ESI) for **$C_{22}H_{24}NBO_2$ $[M+NH_4^+]^+$:** calculated: 324.2215, found: 324.2221.

(4S,5S)-4,5-Diphenyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (3.37)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (47%, 46 mg).

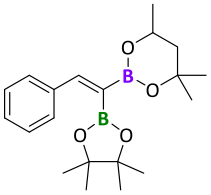
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 – 7.61 (m, 2H), 7.44 – 7.34 (m, 12H), 7.32 – 7.26 (m, 1H), 6.36 (d, *J* = 2.8 Hz, 1H), 6.28 (d, *J* = 2.9 Hz, 1H), 5.31 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.24, 140.40, 133.08, 128.96, 128.53, 128.46, 127.40, 127.37, 125.98, 87.07.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.76.

HRMS (ESI) for **$C_{22}H_{23}NBO_2$ $[M+NH_4^+]^+$:** calculated: 344.1822, found: 344.1834.

(*Z*)-4,4,6-Trimethyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (3.40)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (65%, 48 mg).

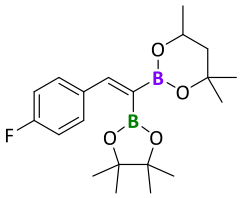
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.53 – 7.41 (m, 2H), 7.32 – 7.19 (m, 3H), 4.26 (m, 1H), 1.76 (dd, *J* = 13.8, 3.0 Hz, 1H), 1.53 (dd, *J* = 13.9, 4.6 Hz, 1H), 1.31 (s, 12H), 1.30 (s, 6H), 1.27 – 1.24 (d, *J* = 11.3, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.57, 140.16, 128.09, 128.02, 127.91, 83.39, 70.85, 64.86, 45.86, 31.28, 28.19, 24.86, 24.74, 23.11.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.11.

HRMS (ESI) for **$C_{20}H_{30}B_2O_4$ [M+H$^+$]$^+$:** calculated: 357.2409, found: 357.2410.

(*Z*)-2-(2-(4-Fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (3.41)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (64%, 57 mg).

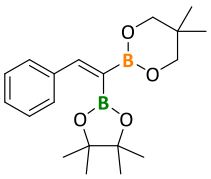
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (s, 1H), 7.47 – 7.40 (m, 2H), 6.97 (m, 2H), 4.24 (m, 1H), 1.76 (dd, *J* = 13.9, 3.0 Hz, 1H), 1.55 – 1.48 (m, 2H), 1.31 (s, 12H), 1.30 (s, 6H), 1.28 – 1.24 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.21, 129.78, 129.70, 115.05, 114.83, 83.46, 70.90, 64.89, 45.85, 31.26, 28.18, 24.85, 24.74, 23.09.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.10.

HRMS (ESI) for **$C_{20}H_{29}B_2FO_4$ [M+H$^+$]$^+$:** calculated: 375.2313, found: 375.2316.

(*Z*)-5,5-Dimethyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (3.42)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (22%, 10 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (s, 1H), 7.51 – 7.46 (m, 2H), 7.33 – 7.22 (m, 3H), 3.67 (s, 4H), 1.30 (s, 12H), 0.98 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.19, 152.97, 139.89, 128.14, 128.07, 83.49, 72.26, 31.81, 24.72, 21.99.

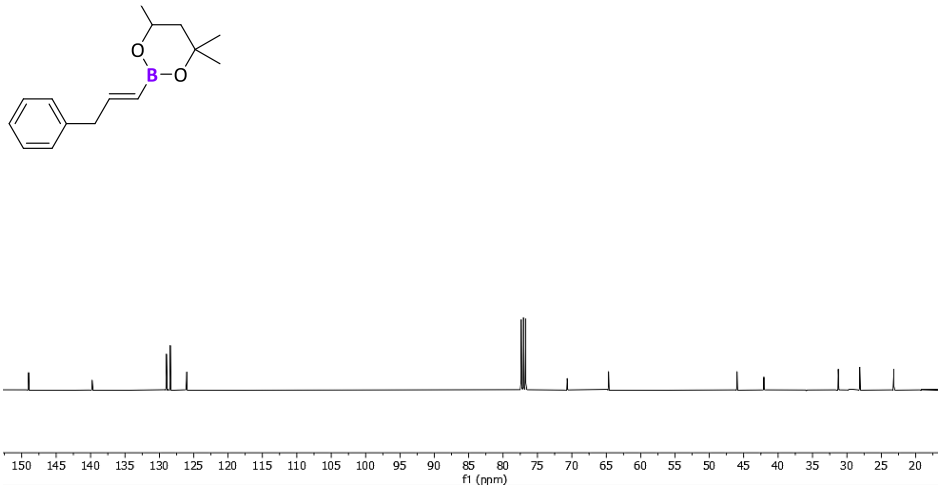
^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.52.

HRMS (ESI) for **$C_{19}H_{28}B_2O_4$ $[M+H^+]^+$:** calculated: 343.2261, found: 343.2270.

- Selected NMR spectra

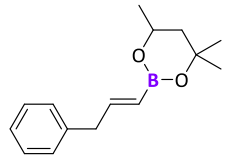
^{1}H- NMR ($CDCl_3$, 400 MHz) ***E*-3.12**

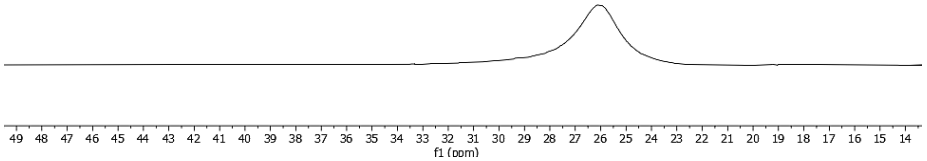
^{13}C- NMR ($CDCl_3$, 100 MHz) ***E*-3.12**

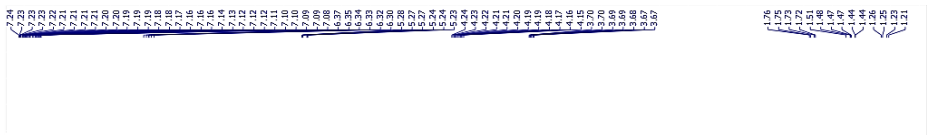


Transborylation of alkenylboranes with diboron reagents

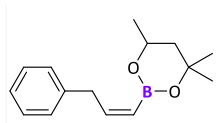
^{11}B- NMR ($CDCl_3$, 128.3 MHz) ***E*-3.12**

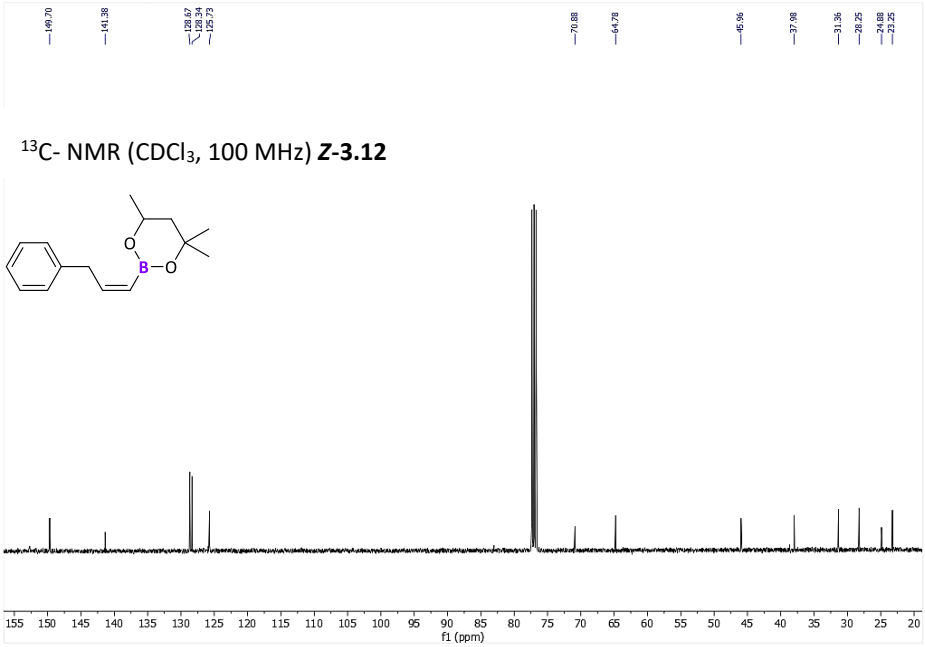




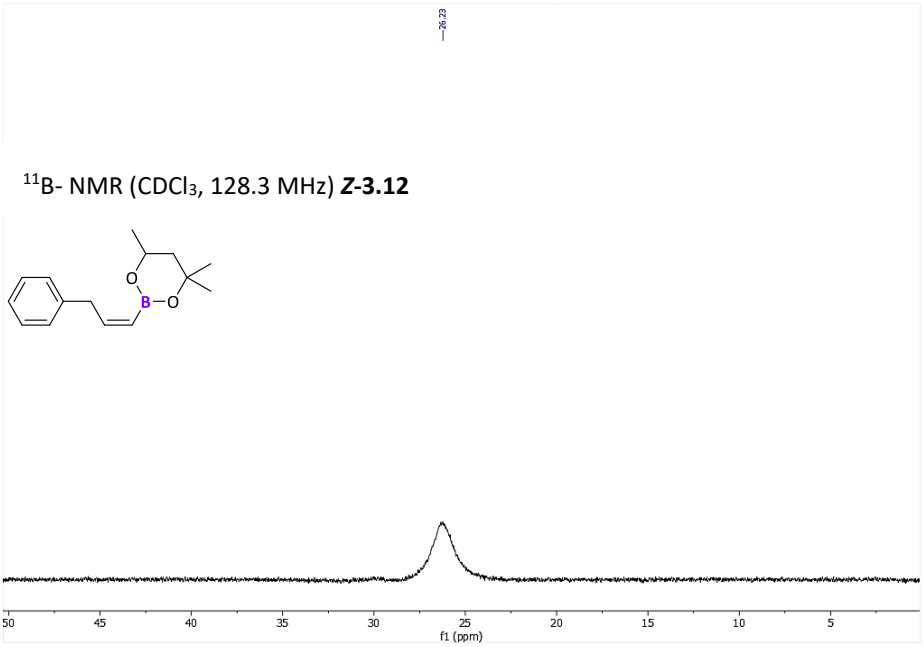


^{1}H- NMR ($CDCl_3$, 400 MHz) ***Z*-3.12**



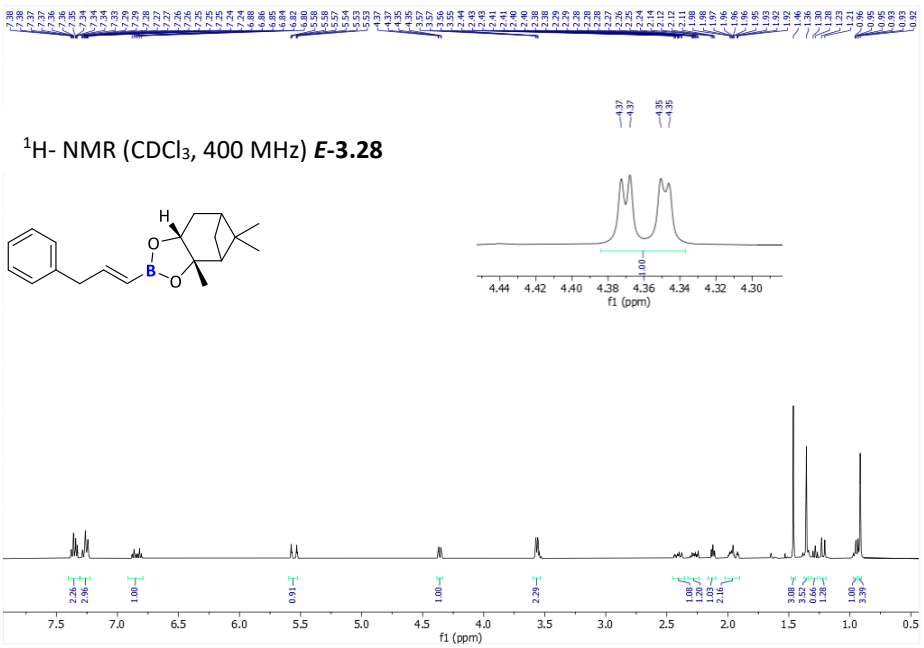


^{13}C- NMR ($CDCl_3$, 100 MHz) ***Z*-3.12**

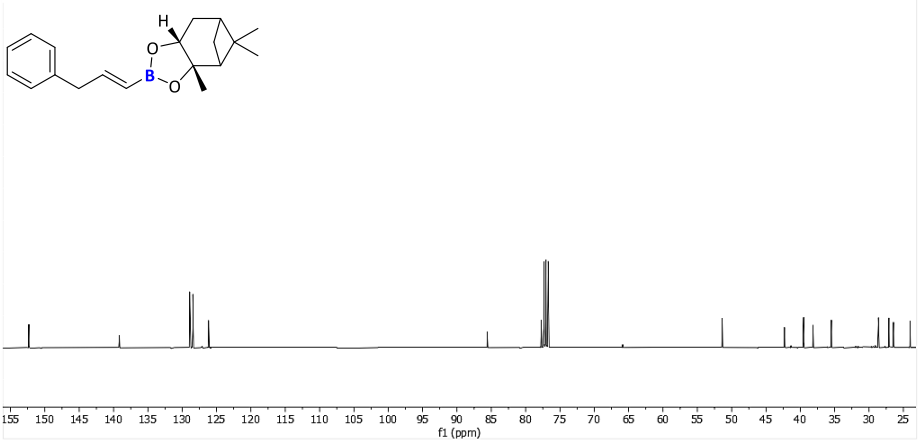


^{11}B- NMR ($CDCl_3$, 128.3 MHz) ***Z*-3.12**

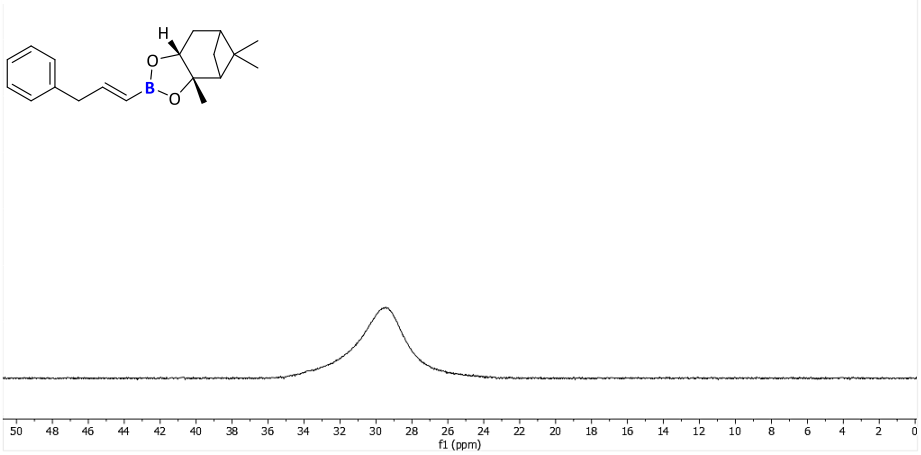
^{1}H- NMR ($CDCl_3$, 400 MHz) ***E*-3.28**



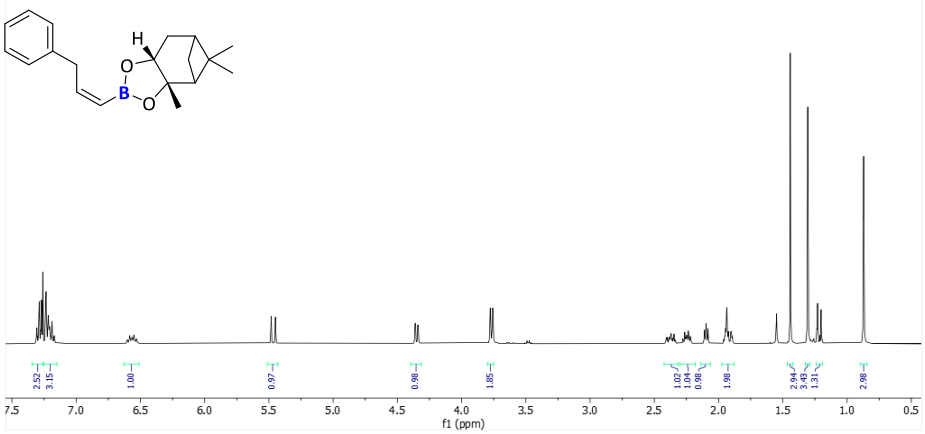
^{13}C- NMR ($CDCl_3$, 100 MHz) ***E*-3.28**



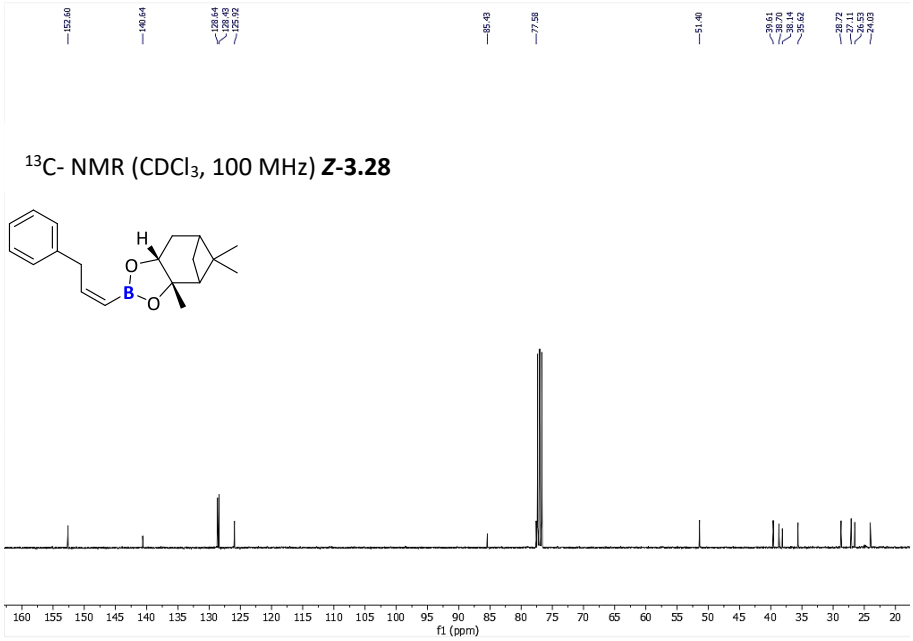
^{11}B- NMR ($CDCl_3$, 128.3 MHz) ***E*-3.28**



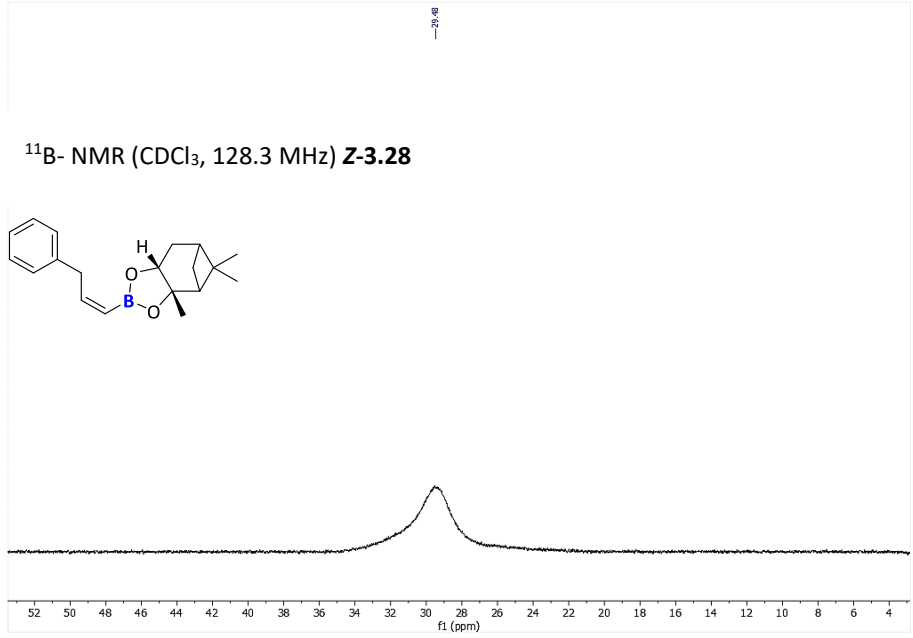
^{1}H- NMR ($CDCl_3$, 400 MHz) ***Z*-3.28**



Transborylation of alkenylboranes with diboron reagents



^{13}C- NMR ($CDCl_3$, 100 MHz) ***Z*-3.28**



^{11}B- NMR ($CDCl_3$, 128.3 MHz) ***Z*-3.28**

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[31] Calculations were performed with Gaussian16 using B97XD and 6-31g(d,p) basis set, and the solvent effects by IEF-PCM model. The optimised structures are available in the ioChem-BD repository via https://doi.org/10.19061/iochem-bd-2-57.

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CHAPTER IV

Cyclopropanation reaction of transborylated alkenylboranes

UNIVERSITAT ROVIRA I VIRGILI
Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

4.1. State of the art

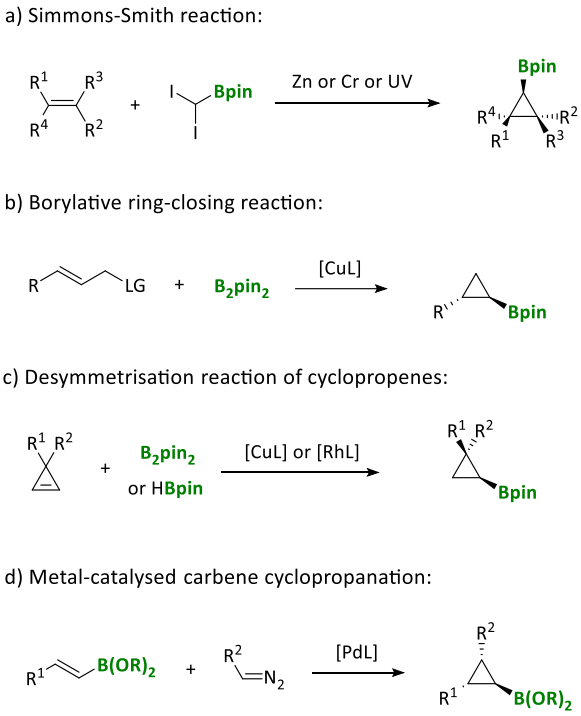
Three-membered carbocycles are found in many biologically important compounds and play a significant role in drug discovery programs.[1] Consequently, stereodefined cyclopropanes are extremely versatile building blocks for organic synthesis. Due to their strained structure and interesting bonding characteristics, the relative distribution of the cyclopropane substituents becomes a crucial point.[2]

Whereas transition metal-assisted transformations of small rings have primarily limited the use of stoichiometric organometallic complexes, nowadays, transition metal-catalysed chemistry of three-membered carbocycles has become a major objective for several research groups worldwide.[3]

4.1.1. Synthesis of cyclopropylboranes

The presence of boryl substituents in cyclopropane rings is increasingly capturing the scientific community's interest, as it offers the potential to transform the cyclopropyl structure into more complex molecules. However, the direct access to cyclopropylboranes, with high levels of diastereoselectivity, remains a significant challenge.[4]

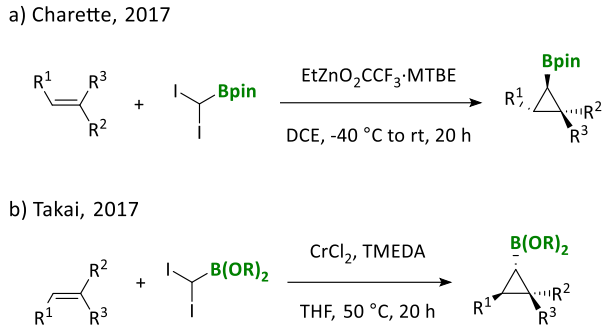
The established methodologies for accessing cyclopropylboranes typically involve the a) Simmons–Smith reaction using boromethylzinc carbenoid, b) borylative ring closure of allylic compounds, c) desymmetrisation of cyclopropenes, and d) metal-catalysed carbene cyclopropanation of vinyl boronic esters (Scheme 4.1).



Scheme 4.1. Direct synthesis of cyclopropylboranes.

The well-known Simmons-Smith reaction is considered a strategic methodology for achieving cyclopropylboranes. In this context, Charette and co-workers developed a direct borocyclopropanation of substituted olefins using borylmethylzinc carbenoids.[5,6] This reaction involved the formation of the cyclopropane ring at the same time as the installation of the boryl moiety, yielding the corresponding borylcyclopropanes with excellent stereocontrol (Scheme 4.2a). Shortly after, Takai and co-workers investigated the reactivity of unactivated alkenes with diiodomethyl boronic esters in the presence of a large excess of $CrCl_2$ and tetramethylethylenediamine (TMEDA) (Scheme 4.2b).[7]

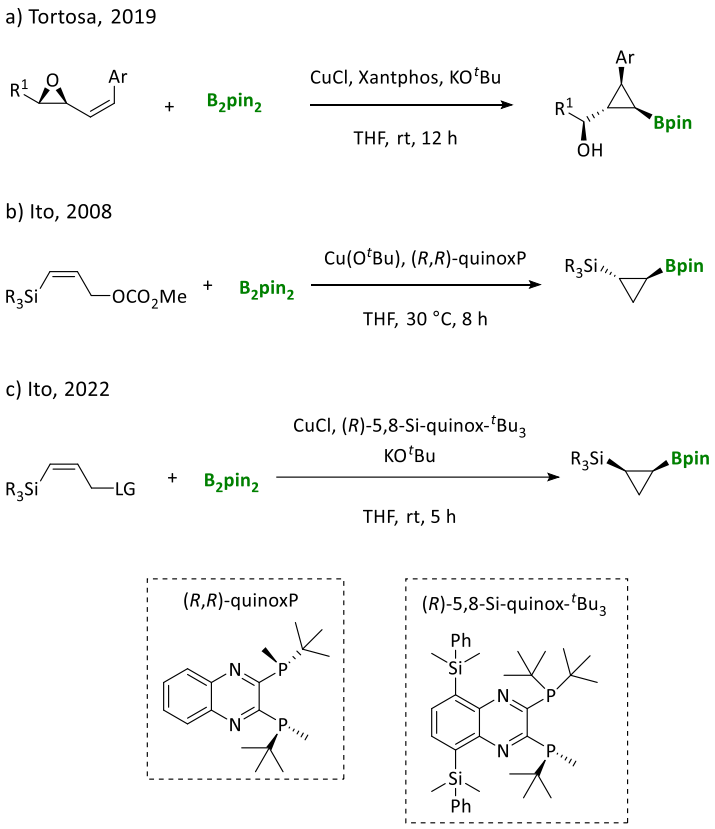
Cyclopropanation reaction of transborylated alkenylboranes



Scheme 4.2. Direct synthesis of cyclopropylboranes through Simmons-Smith reaction.

Alternatively, Tortosa and co-workers have developed a ring-opening/ring-closing reaction of readily available allylic epoxides using an inexpensive Cu(I) source and Xantphos as a ligand, in the presence of B_2pin_2.[8] This reaction proceeded through a borylcupration of the alkene moiety, followed by a subsequent intramolecular S_N2-type reaction, to afford the corresponding cyclopropylboronates with four contiguous stereocenters (Scheme 4.3a).

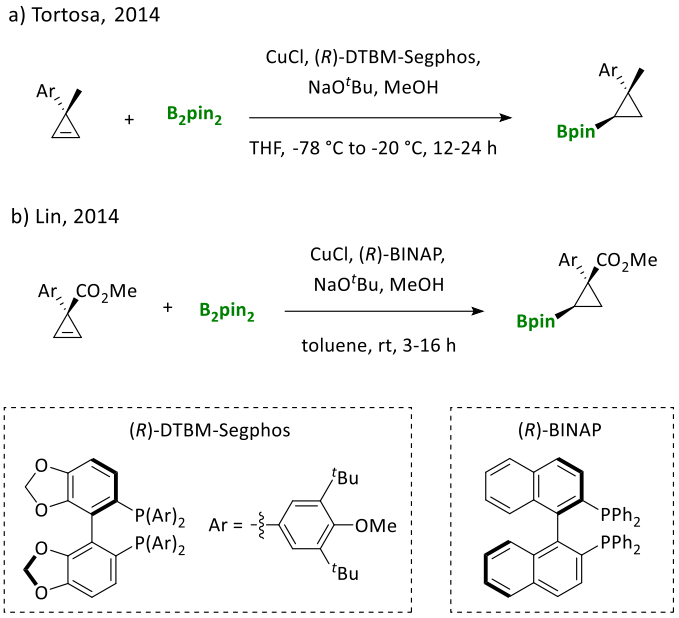
In 2008, Ito and co-workers studied the ring-closing copper(I)-catalysed reaction of γ-silylated allylic carbonates with diboron species to promote the synthesis of B, Si bifunctional cyclopropane derivatives.[9] The reactivity of substituted (*Z*)-vinylsilanes with Cu(O^{t}Bu) and (*R*,*R*)-quinoxP ligand resulted in the formation of *trans*-silyl-substituted cyclopropylboronates with complete stereo and enantiocontrol (Scheme 4.3b). More recently, the same group reported a new asymmetric route by ligand-controlled product switch using (*E*)-allylic phosphates as substrates to afford 1,2-*cis*-silyl-boryl-cyclopropanes (Scheme 4.3c).[10]



Scheme 4.3. Synthesis of cyclopropylboranes through borylative ring closing of allylic compounds.

Furthermore, the desymmetrisation of cyclopropenes has been established as an alternative synthetic strategy for the generation of 3,3-disubstituted cyclopropylboranes. In this context, Tortosa and co-workers reported a copper(I)-catalysed enantioselective hydroboration reaction using (*R*)-DTBM-Segphos as the chiral ligand (Scheme 4.4a).[11] Additionally, the *in-situ* electrophilic trapping of cyclopropylborane with electrophilic amines was also studied using a CuCl/dppf catalyst system.

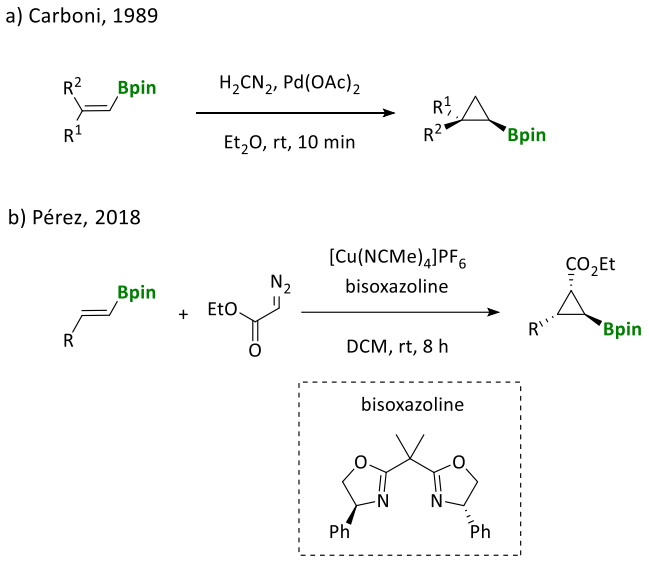
Additionally, a copper(I)-catalysed enantioselective hydroboration of 3-aryl 3-methyl ester substituted cyclopropanes was studied by Lin and co-workers (Scheme 4.4b).[12] The reaction proceeded efficiently using (*R*)-BINAP as the chiral biphosphine ligand.



Scheme 4.4. Direct synthesis of cyclopropylboranes through hydroboration reaction.

On the other hand, the metal-catalysed carbene cyclopropanation of vinyl boronic esters was first studied by Carboni and co-workers in 1989 (Scheme 4.5a).[13] The cyclopropanation was achieved by the addition of a carbene, generated by diazomethane in the presence of palladium acetate using vinyl boronic esters as substrates. However, when other substituted carbenes and/or disubstituted alkenylboranes were used, a *Z*/*E* mixture of cyclopropanes was obtained.[14]

More recently, Pérez and co-workers reported the diastereo- and enantioselective cyclopropanation of alkenylboranes with the presence of ethyl diazoacetate by using a copper(I)/bisoxazoline complex (Scheme 4.5b).[15] The reaction proceeded without the need for any directing group, being the first example of the enantioselective synthesis of 1-boryl-2,3-disubstituted cyclopropanes.



Scheme 4.5. Direct synthesis of cyclopropylboranes through metal-catalysed carbene cyclopropanation reaction.

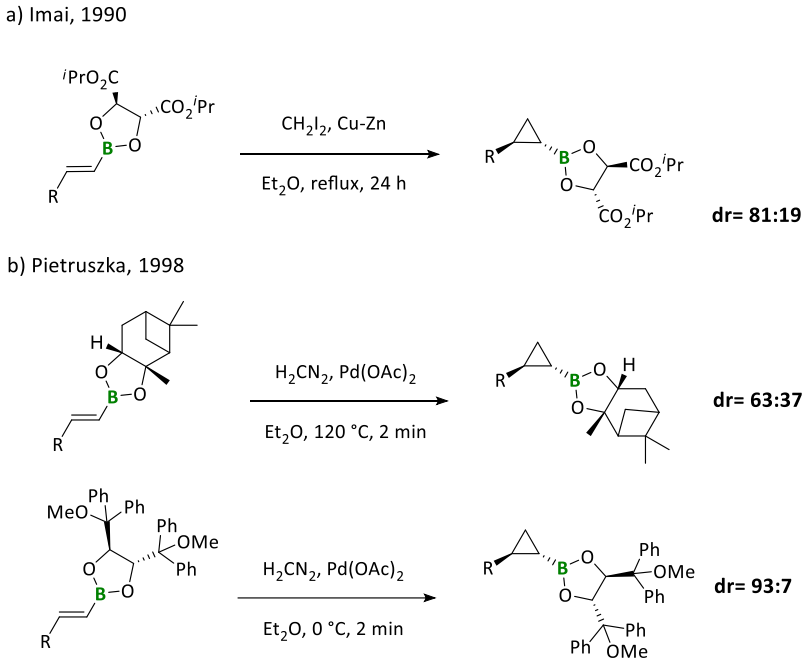
4.1.2. Cyclopropanation reaction of alkenylboranes with chiral boryl moieties

The incorporation of chiral auxiliaries in the well-known boronic esters is a convenient strategy initiated by Imai and co-workers[16] that promotes good diastereoselectivities in the borylcyclopropane products.

In this context, Imai and co-workers reported the first asymmetric cyclopropanation of 1-alkenylboranes by employing inexpensive tartaric acid derivatives as the chiral modifier and Simmons Smith reagent (Scheme 4.6a).[16] In this work, they observed a remarkable diastereoselectivity due to a chelation effect of the Simmons-Smith reagent with the boron moiety.

Alternatively, Pietruszka and co-workers[17] reported the palladium(II)-catalysed diastereoselective cyclopropanation using more stable chiral diols providing high yield and selectivity on the desired products (Scheme 4.6b). Moreover, this flexible approach facilitated the isolation of products with more functionalised side chains investigating the influence of stereogenic centers in diastereoselectivity.[18] The study demonstrated that the reaction's control varied with the cyclopropanation conditions:

it was predominantly substrate-controlled using the Simmons–Smith protocol, while it was auxiliary-controlled with diazomethane–palladium(II) acetate.



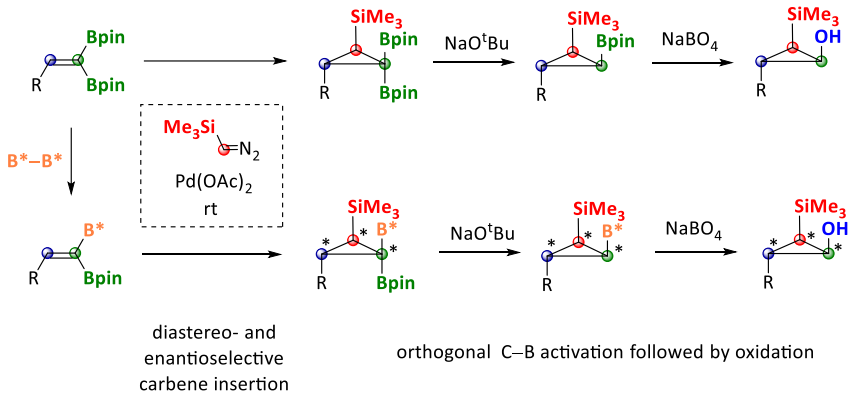
Scheme 4.6. Direct synthesis of cyclopropylboranes with chiral boryl moieties.

4.2. Project aims

With those precedents in mind, we devised a new strategic synthesis of *gem*-bis(boryl)cyclopropanes from the corresponding 1,1-diborylalkenes via Pd-catalysed carbene insertion of (trimethylsilyl)diazomethane (TMSDM) (Scheme 4.7).

The specific objectives are:

- Study of the relative stereoselectivity.
- Influence of mixed 1,1-diborylalkenes towards the stereoselective synthesis of (B,B',Si)-cyclopropanes.
- Selective activation of 1,1-diborylpropanes.
- Synthesis of stereoselective polyfunctional cyclopropyl alcohols.



Scheme 4.7. New strategic synthesis to prepare stereoselective (B, B', Si)-cyclopropanes.

4.3. Results and discussion

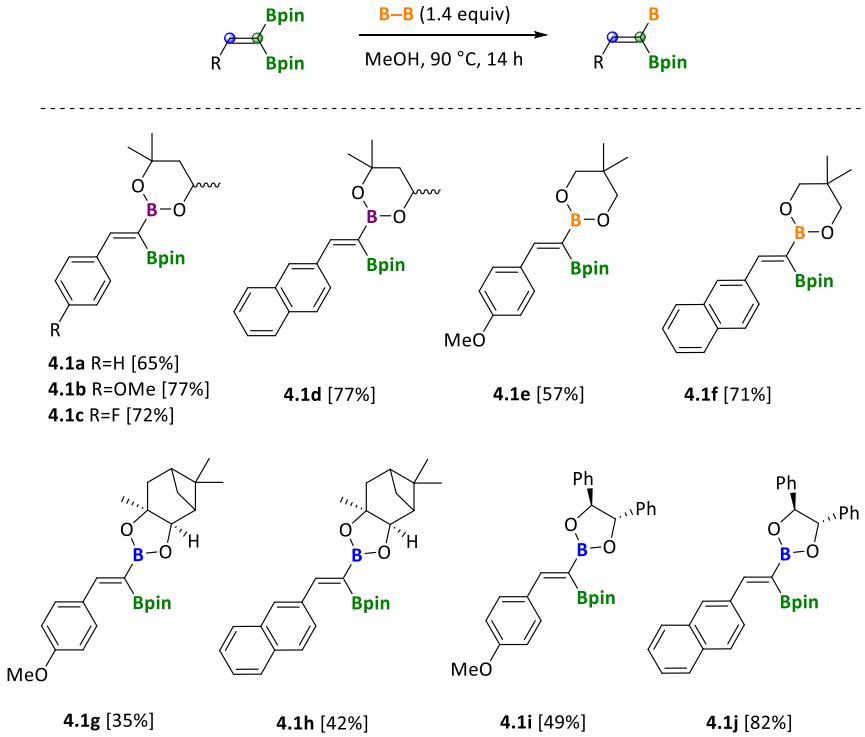
4.3.1. Synthesis of mixed 1,1-diborylalkenes

In this study, we adapted the protocol for the B–C(sp^2)–B/B'–B' cross-metathesis reaction based on our recently developed transborylation sequence of Chapter III.

Consequently, 2-substituted 1,1-bis(pinacolboryl)alkenes were reacted with bis(hexylene glycolato) diboron (B_2hex_2) or bis(neopenthyl glycolato) diboron (B_2neo_2) in MeOH at 90 °C, producing the mixed 2-aryl 1,1-diborylalkenes **4.1a**-**4.1f** (Scheme 4.8). The transborylation occurred stereoselectively at the less sterically hindered position.

Similarly, the transborylation between 1,1-bis(pinacolboryl)alkenes and bis-(+)-pinanediolato diboron (B_2pai_2) or (*4S*,*4'S*,*5S*,*5'S*)-4,4',5,5'-tetraphenyl-2,2'-bi(1,3,2-dioxaborolane) ((*S*,*S*)-B_2(O-CHPh-CHPh-O)$_2$) was conducted, yielding the chiral mixed 2-aryl 1,1-diborylalkenes **4.1g**-**4.1j** (Scheme 4.8).

In all cases, moderate to high yields were observed, but the most remarkable issue was that the transborylation took place stereoselectively in the Bpin moiety *trans* to the aryl group. This particular stereocontrol was assumed to proceed since this Bpin moiety is less sterically hindered to be involved in the transborylation reaction.



Scheme 4.8. Substrate scope for transborylation reaction of 1,1-diborylalkenes with diboron reagents. Isolated yields in brackets.

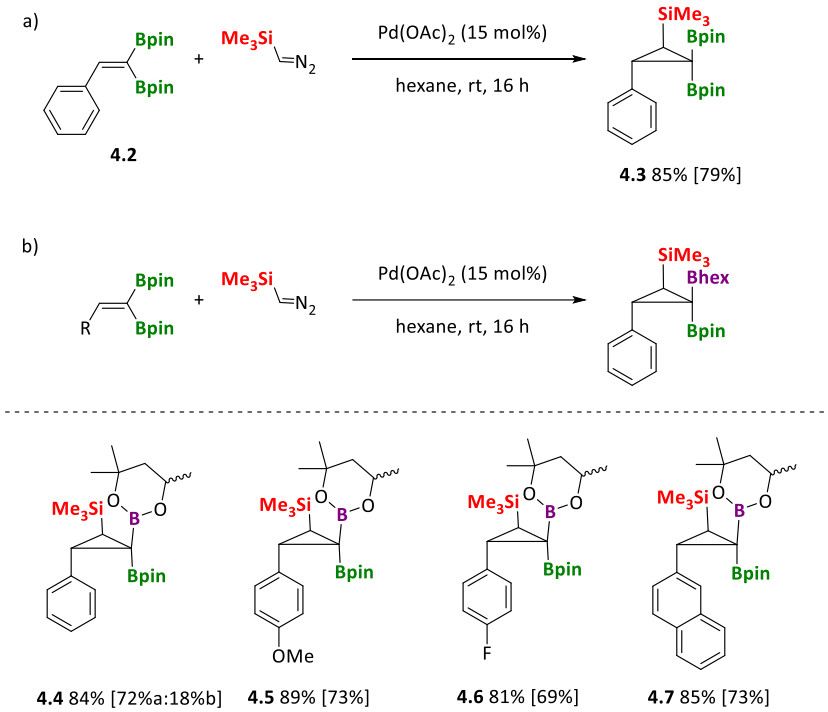
4.3.2. Stereoselective cyclopropanation of mixed 1,1-diborylalkenes

We next investigated the Pd-catalysed cyclopropanation using (trimethylsilyl)diazomethane (TMSDM) as the carbene source. This addition aimed to produce polyfunctionalised 1,1-diboryl-2-silylcyclopropanes. The 1,1-diborylalkene **4.2** was chosen as the model substrate to demonstrate the proof of concept. The reaction was carried out with 1 equivalent of **4.2** and 7 equivalents of TMSDM in the presence of 15 mol% of $Pd(OAc)_2$, in hexane at room temperature. The reaction was completed within 16 hours, with total stereoselective control, yielding the new product **4.3** where the trimethylsilyl and phenyl groups were positioned in a relative *anti*-conformation (Scheme 4.9).

We next envisaged the palladium-catalysed stereoselective cyclopropanation extending the reactivity to the mixed 1,1-(BpinBhex)alkenes **4.1a**-**4.1d** with TMSDM. This resulted in high stereoselectivity, providing one exclusive conformer in which the

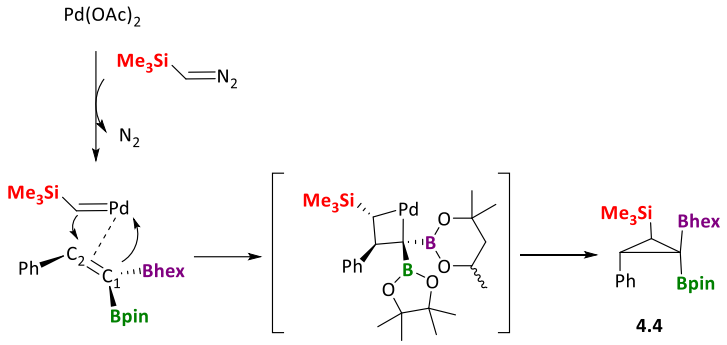
Bhex moiety appears *syn* to the trimethylsilyl group, whereas the Bpin fragment is placed *syn* to the aryl group, for all compounds **4.4**-**4.7** (Scheme 4.9).

The diastereoselectivity was unambiguously determined through 1D-NMR NOE experiments. Interestingly, product **4.4**, would be isolated as both isomers based on the Me conformation on the Bhex group.



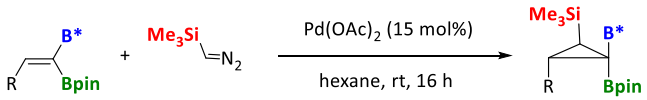
Scheme 4.9. Substrate scope for cyclopropanation reaction of 1,1-diborylalkene substrates with B_2hex_2. NMR yield was determined with naphthalene as the internal standard. Isolated yields in brackets.

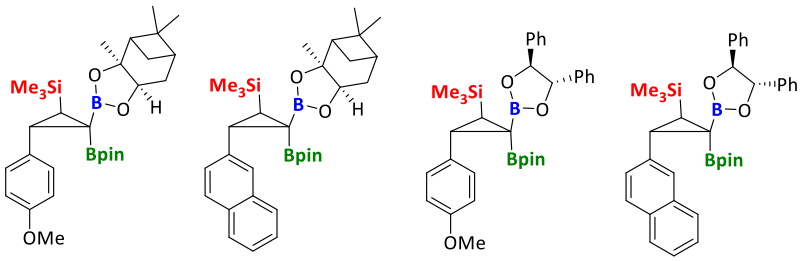
We have suggested a mechanism for the palladium-catalysed cyclopropanation reaction with mixed 1,1-(BpinBhex)alkenes. Firstly, the reaction might proceed through the formation of the palladium carbene, with the subsequent release of nitrogen, followed by the migratory insertion of Pd=CH–TMS into the trisubstituted alkene. Subsequently, the corresponding B, B', Si cyclopropane **4.4** might be formed exclusively with *anti*-conformation between the $SiMe_3$ and the phenyl group, and the Bpin fragment placed *syn* to the aryl group (Scheme 4.10).



Scheme 4.10. Suggested mechanistic model for Pd-catalysed cyclopropanation reaction of **4.4**.

We next conducted the Pd-catalysed cyclopropanation of the mixed chiral 1,1-(Bpin,B*)-alkenes **4.1g**-**4.1j** with TMSDM (B* = Bpai = (+)-pinanediolboryl, or (*S*,*S*)-B_2(O-CHPh-CHPh-O)$_2$). Under optimised conditions, the corresponding (B*,Bpin,Si)-cyclopropanes **4.8**-**4.11** were isolated as unique isomers (Scheme 4.11). This contrasted with the reported Pd-catalysed cyclopropanation of alkenylboranes containing Bpai motifs, using diazomethane as the carbene source, which provided a modest diastereoselection of up to 63:37.[17a]



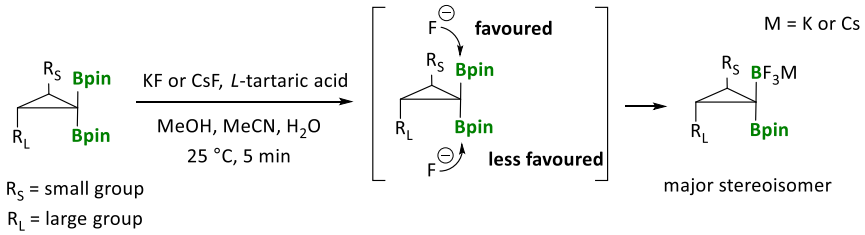


4.8 92% [86%] **4.9** 98% [94%] **4.10** 95% [86%] **4.11** 89% [81%]

Scheme 4.11. Substrate scope for cyclopropanation reaction of 1,1-diborylalkene substrates with chiral diboron reagents. NMR yield was determined with naphthalene as the internal standard. Isolated yields in brackets.

4.3.3. Orthogonal functionalisation of (B, B, Si)-cyclopropanes

It is worth mentioning, for comparison, that Masarwa and co-workers proposed a complementary diastereoselective model for the desymmetrisation of *gem*-bis(pinacolboryl)cyclopropanes via nucleophilic trifluorination reaction of the Bpin group.[19,20] The desymmetrisation reaction was performed with KF or CsF, in the presence of a slight excess of *L*-tartaric acid, in methanol and acetonitrile, towards the formation of trifluorinated boron salt on the less steric hindered Bpin moiety (Scheme 4.12).

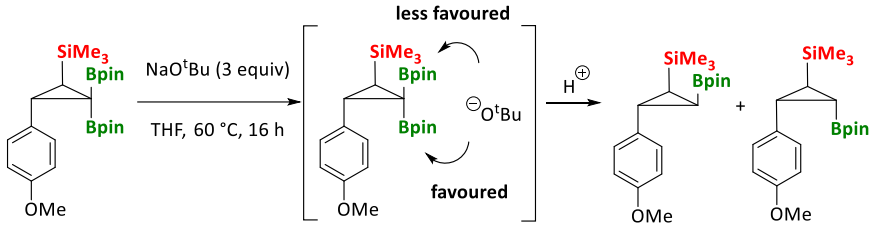


Scheme 4.12. Diastereoselective desymmetrisation of *gem*-diborylcyclopropanes.

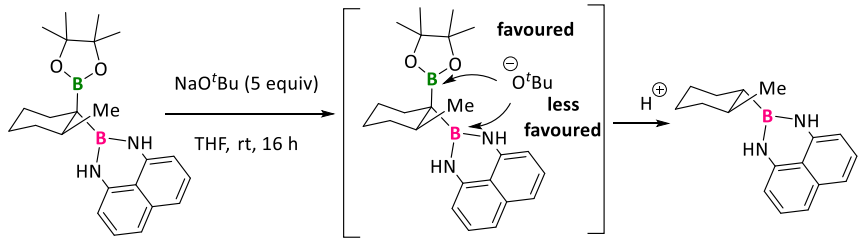
In this context, the orthogonal functionalisation of the (B, B', Si)-cyclopropanes, prepared in this work, became our next objective. When we applied the protodeborylation protocol by using 3 equivalents of NaO^{t}Bu at 60 °C on the model (B, B', Si)-cyclopropane **4.12**, it was observed the preferred activation of the Bpin moiety placed in *syn*-conformation to the aryl group, generating **4.13a** in 80% isolated yield (Scheme 4.13a). We suggested that the $SiMe_3$ group acts as a protecting group of the *syn* vicinal Bpin moiety, whereas the Ph group has a lower protecting role *versus* the protodeborylation step.

This hypothesis contrasted with the selective alkoxide-assisted protodeborylation of *gem*-BpinBdan-cyclohexanes, which was based on the differing electronic properties of the boryl groups. The alkoxy group interacted preferentially with the Bpin moiety forming a stable Lewis acid-base adduct that evolved towards the stabilised carbanion that was characterised by the strong delocalisation into the π-channel of the α-Bdan moiety (Scheme 4.13b).[21]

a) Protodeborylation of (B, B, Si)-cyclopropanes:



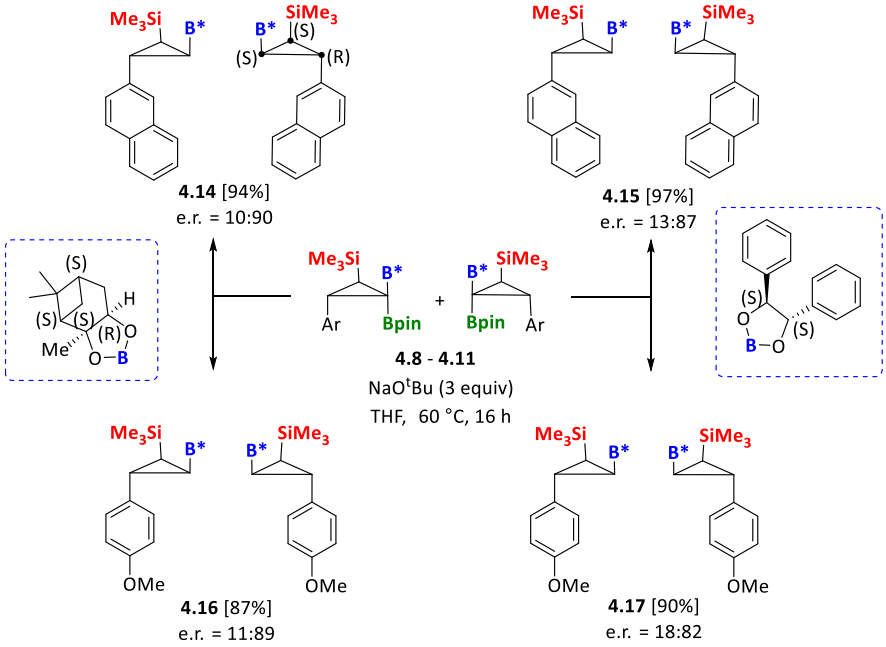
b) Precedents on selective protodeborylation of mixed *gem*-diborylcycloalkanes:



Scheme 4.13. Site-selective protodeborylation of *gem*-bis(boryl)cyclopropanes and *gem*-bis(boryl)cyclohexanes. NMR yield was determined with naphthalene as the internal standard. Isolated yields in brackets.

A similar trend was observed when the (B*, B, Si)-cyclopropanes **4.8**-**4.11**, containing the chiral boryl units B*= (+)-pinanediolboryl (Bpai), or (*S,S*)-B_2(O-CHPh-CHPh-O)$_2$, also reacted with NaO^{t}Bu under the same conditions, generating the products **4.14**-**4.17**, showing the exclusive protodeborylation of the Bpin unit (Scheme 4.14).

The X-ray single-crystal diffraction analysis of compound **4.14** revealed the absolute configuration of the three new stereocenters formed in the major enantiomer (Figure 4.1). The enantiomeric ratio was determined from the corresponding alcohol derivatives after oxidising the (B*, Si)-cyclopropanes **4.14**-**4.17** with NaO^{t}Bu, compared to the racemic samples. The enantiomeric ratio appeared to be slightly higher when B* was (+)-pinanediolboryl (Bpai) rather than (*S,S*)-B_2(O-CHPh-CHPh-O)$_2$, regardless of the aryl group present in the compounds. This difference was likely due to more efficient asymmetric induction during the palladium insertion of TMSDM into the chiral mixed 2-aryl 1,1-diborylalkenes **4.1g**, **4.1h** versus **4.1i**, **4.1j**.



Scheme 4.14. Protodeborylation of (B*,B,Si)-cyclopropanes affording enantioenriched (B*,Si)-cyclopropane compounds. Isolated yield shown in brackets. (e.r. determined by HPLC on the corresponding enantioenriched mixture of the oxidised samples **4.18** and **4.19**).

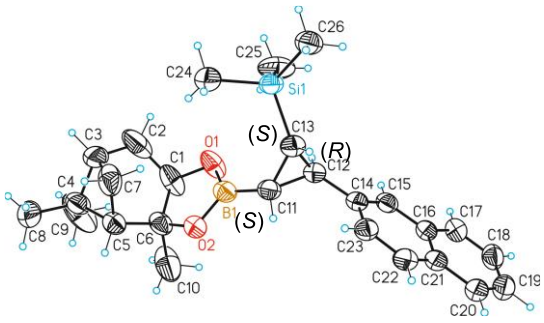


Figure 4.1. X-Ray single-crystal diffraction analysis of major enantiomer of compound **4.14**. (Thermal ellipsoids draw at 50% level).

4.4. Conclusions

In conclusion, we have described a new palladium-catalysed cyclopropanation of 2-substituted 1,1-diborylalkenes with (trimethylsilyl)diazomethane (TMSDM). Our method contributed to preparing stereoselective *gem*-bis(boryl)cyclopropanes containing different boryl moieties, as an alternative to reported methods.

The relative stereoselectivity was controlled via carbene insertion sequence generating an exclusive *anti*-conformation between the vicinal R and $SiMe_3$ substituents on the new (B, B, Si)-cyclopropanes. Additionally, the stereoselective (B*,B,Si)-cyclopropanes could be activated by NaO^tBu, via protodeborylation preferentially on the boron moiety *syn* to the aryl group.

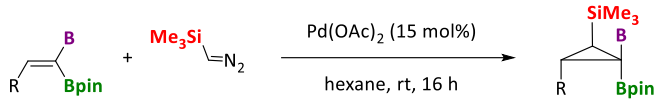
Furthermore, an enantiomeric ratio of up to 10:90 was achieved when B* = (+)-pinanediolboryl (Bpai) was employed as a chiral auxiliary in 1,1-diborylalkenes, determining the absolute configuration of the three new stereocenters formed in the major enantiomer.

4.5. Experimental section

General information. All solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures.[22] Diboron reagents were purchased from Dalian Allychem Co. and were used without further purification. All air-sensitive reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon using Schlenk-type techniques. Flash chromatography purification procedures were performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Analytical Thin Layer Chromatography (TLC) was performed on Merck Kieselgel 60 F254 and was developed using standard visualising agents: UV fluorescence (254 and 366 nm) or potassium permanganate. NMR spectra were recorded at a Varian 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm ^{1}H and 77.16 ppm ^{13}C). ^{11}B NMR chemical shifts (δ) are reported in ppm relative to $BF_3{\cdot}Et_2O$. Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sp = septet, m = multiplet. Melting points were measured using open glass capillaries in a Digital Melting Point IA 9100 apparatus. High-Resolution Mass Spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies with an ESI interface that is located at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona), or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or EI interface that is located at the Unidade de Espectrometría de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela). GC-MS analyses were performed on an 8860 GC System with a 5977B GC/MSD from Agilent Technologies equipped with a capillary column HP-5MS Ultra Inert (30 m, 0.25 mm i.d., 0.25 µm thickness) and using He as the carrier gas. GC-MS analyses were performed on an 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. Crystal structure determinations for sample **PD392** was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using

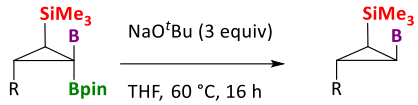
CuK$_\alpha$ radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used*: Data collection APEX-2,[23] data reduction Bruker Saint[24] V/.60A and absorption correction TWINABS.[25]

General procedure for the cyclopropanation of 1,1-diborylalkenes



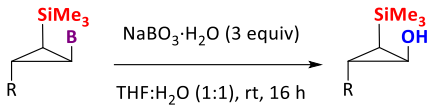
In a glove box, a Schlenk-tube equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (15 mol%). Then the 1,1-diborylalkene substrate (0.2 mmol, 1 equiv) and hexane (1mL) were added. The mixture was stirred for 5 minutes and the (diazomethyl)trimethylsilane 2M (1.4 mmol, 7 equiv) was added dropwise and the reaction was stirred for 5 minutes in the glovebox. The Schlenk-tube was closed with a Teflon cap and was allowed to react for 16 h at room temperature, with magnetic stirring. The mixture was filtered through Celite and washed with Et_2O. 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.

General procedure for the protodeborylation of 1,1-diborylcyclopropanes



A Schlenk-tube equipped with a magnetic stir bar was charged with NaO^tBu (0.6 mmol, 3 equiv), the corresponding 1,1-diborylcyclopropane (0.2 mmol, 1 equiv) and THF (2 mL). The Schlenk-tube was closed with a Teflon cap and the reaction was stirred for 16 h at 60 °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.

General procedure for the oxidation of borylcyclopropanes (to determine the e.r. by HPLC)



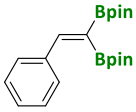
In an opened-air flask, charged with a magnetic stir bar, were added the corresponding borylcyclopropane (0.1 mmol, 1 equiv), $NaBO_3{\cdot}H_2O$ (0.3 mmol, 3 equiv), THF (2 mL) and distilled water (1 mL). The reaction was closed with a septum with a needle to avoid over pressure and was stirred for 16 h at room temperature. After this time, the mixture was extracted with Et_2O (3 x 15 mL), the organic layer was dried with anhydrous magnesium sulphate and filtered. 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.

X-Ray single-crystal diffraction analysis for 4.14

Method for crystal growth: a saturated solution of 5-10 mg of solid in 0.1 mL of dichloromethane was prepared in a 2 mL GC-vial. 1 mL of pentane was then carefully added forming two layers. The system was then allowed to slowly evaporate with a needle in the cap until the crystals were obtained. Ortep-Drawing (thermal ellipsoids draw at 50% level) in two orientations.

- Characterisation data for 4.2

2,2'-(2-phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4.2)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:3). The product was isolated as a pale yellowish oil (58%, 41 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (s, 1H), 7.51 – 7.44 (m, 2H), 7.34 – 7.27 (m, 3H), 1.31 (s, 12H), 1.28 (s, 12H).

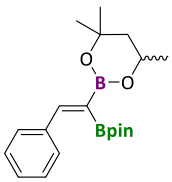
^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 139.6, 128.4, 128.2, 128.1, 83.6, 83.2, 24.8, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.8.

HRMS (ESI) for **$C_{20}H_{30}B_2O_4$ [M+H]$^+$:** calculated: 371.2568, found: 371.2567.

- Characterisation data for transborylated alkenylboranes

(*Z*)-4,4,6-Trimethyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (4.1a)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (65%, 47 mg).

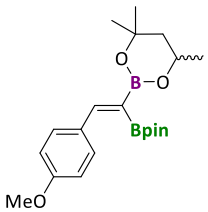
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.53 – 7.41 (m, 2H), 7.32 – 7.19 (m, 3H), 4.26 (m, 1H), 1.76 (dd, J = 13.8, 3.0 Hz, 1H), 1.53 (dd, J = 13.9, 5.6 Hz, 1H), 1.31 (s, 12H), 1.30 (s, 6H), 1.27 – 1.24 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 140.1, 128.0, 128.0, 127.9, 83.3, 70.8, 64.8, 45.8, 31.2, 28.1, 24.8, 24.7, 23.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.1.

HRMS (ESI) for **$C_{20}H_{30}B_2O_4$ [M+H]$^+$:** calculated: 357.2409, found: 357.2410.

(*Z*)-2-(2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4.1b)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (77%, 60 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (s, 1H), 7.46 – 7.39 (m, 2H), 6.85 – 6.75 (m, 2H), 4.24 (m, 1H), 3.79 (s, 3H), 1.78 – 1.70 (m, 1H), 1.56 – 1.47 (m, 2H), 1.32 (s, 12H), 1.29 (s, 6H), 1.26 (s, 3H).

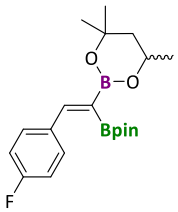
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 152.1, 133.0, 129.5, 113.3, 83.3, 70.7, 64.7, 55.2, 45.8, 31.3, 28.1, 24.9, 24.7, 23.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.1.

HRMS (ESI) for **$C_{21}H_{32}B_2O_5$ [M+H]$^+$:** calculated: 386.0966, found: 386.0959.

Melting point: 62.4 °C.

(*Z*)-4,4,6-Trimethyl-2-(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (4.1c)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (72%, 54 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (s, 1H), 7.47 – 7.41 (m, 2H), 6.99 – 6.92 (m, 2H), 4.25 (m, 1H), 1.76 (dd, J = 13.8, 2.9 Hz, 1H), 1.56 – 1.47 (m, 2H), 1.31 (s, 12H), 1.30 (s, 6H), 1.26 (d, J = 6.1 Hz, 3H).

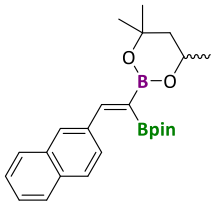
^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.2, 129.7, 129.7, 115.0, 114.8, 83.4, 70.9, 64.8, 45.8, 31.2, 28.1, 24.8, 24.7, 23.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.5, 26.7.

HRMS (ESI) for **$C_{20}H_{30}B_2FO_4$ [M+H]$^+$:** calculated: 375.2314, found: 375.2311.

Melting point: 71.4 °C.

(*Z*)-4,4,6-Trimethyl-2-(2-(naphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (4.1d)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (77%, 63 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 1.7 Hz, 1H), 7.83 – 7.72 (m, 4H), 7.63 (dd, J = 8.5, 1.8 Hz, 1H), 7.47 – 7.41 (m, 2H), 4.28 (m, 1H), 1.78 (dd, J = 13.8, 3.0 Hz, 1H), 1.55 (s, 1H), 1.33 (s, 12H), 1.32 (s, 6H), 1.28 (d, J = 6.2 Hz, 3H).

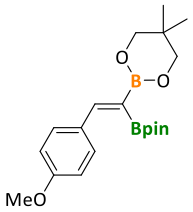
^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 137.8, 133.3, 133.1, 128.2, 127.6, 127.5, 127.3, 126.1, 125.9, 125.9, 83.4, 70.9, 64.9, 45.8, 31.3, 28.2, 24.9, 24.8, 23.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6, 27.0.

HRMS (ESI) for **$C_{24}H_{33}B_2O_4$ [M+H]$^+$:** calculated: 407.2566, found: 407.2568.

Melting point: 63.4 °C.

(*Z*)-2-(2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-5,5-dimethyl-1,3,2-dioxaborinane (4.1e)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (57%, 42 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (s, 1H), 7.43 (d, J = 8.8 Hz, 2H), 6.87 – 6.78 (m, 2H), 3.80 (s, 3H), 3.66 (s, H), 1.32 (s, 12H), 0.98 (s, 6H).

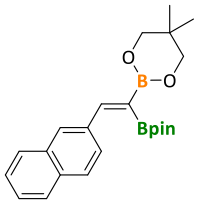
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 152.5, 129.6, 113.4, 83.4, 72.2, 55.2, 31.6, 24.7, 22.6, 22.0, 14.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.7, 26.9.

HRMS (ESI) for **$C_{20}H_{31}B_2O_5$ [M+H]$^+$:** calculated: 373.2357, found: 373.2360.

Melting point: 61.2 °C.

(*Z*)-5,5-Dimethyl-2-(2-(naphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-1,3,2-dioxaborinane (4.1f)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (71%, 55 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 – 7.94 (m, 1H), 7.86 – 7.71 (m, 3H), 7.63 (dd, J = 8.5, 1.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 3.69 (s, 4H), 1.33 (s, 12H), 1.00 (s, 6H).

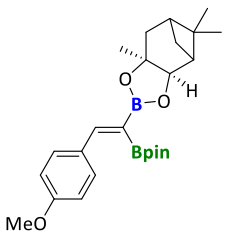
^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.9, 137.5, 133.3, 133.2, 128.2, 127.6, 127.4, 126.1, 126.0, 126.0, 83.5, 72.3, 31.8, 24.8, 22.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.6, 27.1.

HRMS (ESI) for **$C_{23}H_{31}B_2O_4$ [M+H]$^+$:** calculated: 393.2408, found: 393.2409.

Melting point: 70.1 °C.

(*E*)-2-(2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (4.1g)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (35%, 32 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (s, 1H), 7.49 – 7.41 (m, 2H), 6.86 – 6.78 (m, 2H), 4.34 (dd, J = 8.7, 1.9 Hz, 1H), 3.80 (s, 3H), 2.34 (dddd, J = 14.5, 8.7, 3.7, 2.1 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.10 – 2.03 (m, 1H), 1.96 – 1.80 (m, 2H), 1.41 (s, 3H), 1.33 (s, 12H), 1.29 (s, 3H), 1.27 – 1.21 (m, 1H), 0.85 (s, 3H).

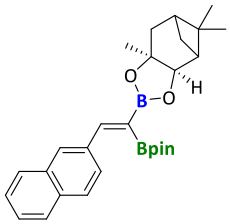
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.9, 155.0, 132.4, 129.8, 113.5, 85.4, 83.5, 77.8, 55.2, 51.4, 39.5, 38.1, 35.6, 28.6, 27.1, 26.4, 24.8, 24.6, 24.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.4.

HRMS (ESI) for **$C_{25}H_{36}B_2O_5$ [M+H]$^+$:** calculated: 439.1726, found: 439.1724.

Melting point: 75.8 °C.

(*Z*)-3a,5,5-Trimethyl-2-(2-(naphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (4.1h)



The product was purified by flash chromatography using as eluent a mixture of hexane/diethyl ether (100:1). The product was isolated as a pale yellowish solid (42%, 39 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (t, J = 2.1 Hz, 1H), 7.90 (s, 1H), 7.81 – 7.74 (m, 3H), 7.64 (dt, J = 8.7, 1.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 4.38 (dd, J = 8.7, 1.9 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.21 – 2.16 (m, 1H), 2.10 – 2.05 (m, 1H), 1.93 – 1.88 (m, 2H), 1.44 (s, 3H), 1.34 (s, 12H), 1.12 (d, J = 10.9 Hz, 2H), 0.90 (s, 3H).

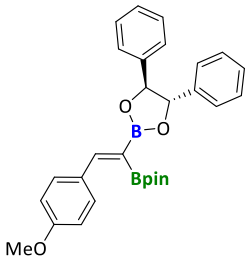
^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 137.2, 133.4, 133.2, 128.3, 127.7, 127.7, 127.6, 126.2, 126.1, 125.9, 85.6, 83.7, 77.9, 51.4, 38.1, 35.6, 34.1, 28.6, 27.1, 26.5, 24.8, 24.7, 24.0, 22.3, 14.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.2.

HRMS (ESI) for **$C_{28}H_{36}B_2O_4$ [M+H]$^+$:** calculated: 459.2876, found: 459.2882.

Melting point: 83.0 °C.

2-((*Z*)-1-((4*S*,5*R*)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-2-(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.1i)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (49%, 47 mg).

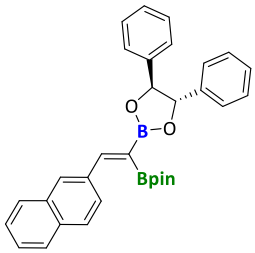
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.57 – 7.48 (m, 2H), 7.44 – 7.28 (m, 10H), 6.87 (d, J = 8.8 Hz, 2H), 5.20 (s, 2H), 3.83 (s, 3H), 1.35 (d, J = 2.3 Hz, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 157.1, 140.7, 130.0, 128.6, 128.1, 125.7, 113.6, 86.4, 83.8, 55.3, 24.9, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.8.

HRMS (ESI) for **$C_{29}H_{33}B_2O_5^+[M+H^+]^+$:** calculated: 483.2512, found: 483.2513.

2-((*Z*)-1-((4*S*,5*R*)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-2-(naphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.1j)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (100:1). The product was isolated as a pale yellowish oil (82%, 82 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (s, 1H), 8.05 – 8.00 (m, 1H), 7.86 – 7.77 (m, 3H), 7.70 (dd, J = 8.6, 1.8 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.32 (m, 10H), 5.25 (s, 2H), 1.37 (s, 16H), 1.36 (s, 16H).

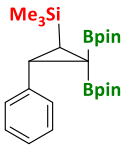
^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 140.6, 128.7, 128.1, 128.1, 126.9, 125.7, 86.5, 84.0, 79.1, 25.0, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.1.

HRMS (ESI) for **$C_{32}H_{32}B_2O_4Na^+[M+Na]^+$:** calculated: 525.2384, found: 525.2387.

- Characterisation data for (B*, B, Si)-cyclopropanes

Trimethyl(3-phenyl-2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)silane (4.3)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (100:3). The product was isolated as a pale yellowish solid (79%, 70 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.15 (m, 2H), 7.13 – 7.04 (m, 1H), 2.46 (d, J = 7.2 Hz, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 0.97 (s, 6H), 0.92 (d, J = 7.2 Hz, 1H), 0.81 (s, 6H), 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 129.0, 127.7, 125.8, 83.1, 82.9, 30.6, 25.3, 25.1, 25.1, 24.2, 14.2, -0.6.

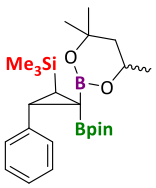
^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.9.

HRMS (ESI) for **$C_{24}H_{41}B_2O_4Si^+[M+H^+]^+$:** calculated: 443.2960, found: 443.2966.

Melting point: 74.7 °C.

Cyclopropane 4.4 has been isolated in both diastereoisomers 4.4a and 4.4b:

(-3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)cyclopropyl)trimethylsilane (4.4a)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (54%, 48 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 – 7.24 (m, 2H), 7.21 – 7.15 (m, 2H), 7.10 – 7.05 (m, 1H), 4.26 – 4.13 (m, 1H), 2.44 (d, J = 7.1 Hz, 1H), 1.71 (dd, J = 13.8, 3.0 Hz, 1H), 1.56 – 1.45 (m, 1H), 1.27 (s, 3H), 1.25 (s, 3H), 1.22 (d, J = 7.1 Hz, 3H), 0.98 (s, 6H), 0.86 (s, 6H), 0.83 (d, J = 7.1 Hz, 1H), 0.08 (s, 9H).

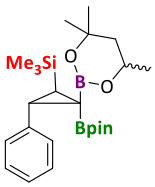
^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.1, 128.6, 127.7, 125.5, 82.7, 70.6, 64.8, 45.7, 31.4, 30.0, 28.3, 25.1, 24.2, 23.1, 14.2, -0.3.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.0, 28.5.

HRMS (ESI) for **$C_{24}H_{41}B_2O_4Si^+[M+H^+]^+$:** calculated: 443.2960, found: 443.2969.

Melting point: 74.5 °C.

(-3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)cyclopropyl)trimethylsilane (4.4b)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (18%, 16 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 – 7.21 (m, 2H), 7.22 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 4.14 – 4.01 (m, 1H), 2.48 (d, J = 7.2 Hz, 1H), 1.70 (dd, J = 14.0, 2.9 Hz, 1H), 1.53 (dd, J = 14.0, 11.5 Hz, 1H), 1.25 (s, 6H), 1.21 (d, J = 7.2 Hz, 3H), 0.97 (s, 6H), 0.88 (s, 6H), 0.83 (d, J = 7.2 Hz, 1H), 0.08 (s, 9H).

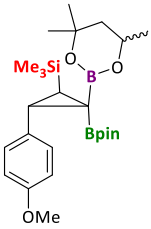
^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 128.5, 127.7, 125.5, 82.6, 70.7, 64.4, 45.7, 31.4, 30.4, 28.5, 25.0, 24.2, 23.1, 14.5, -0.20.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.1, 29.2.

HRMS (ESI) for **$C_{24}H_{41}B_2O_4Si^+[M+H^+]^+$:** calculated: 443.2960, found: 443.2963.

Melting point: 74.5 °C.

(-3-(4-Methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)cyclopropyl)trimethylsilane (4.5)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (73%, 69 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 6.5 Hz, 2H), 4.24 – 4.13 (m, 1H), 3.74 (s, 3H), 2.38 (d, J = 7.2 Hz, 1H), 1.70 (dt, J = 13.7, 3.1 Hz, 1H), 1.55 – 1.43 (m, 1H), 1.26 (s, 3H), 1.26 – 1.22 (m, 3H), 1.21 (t, J = 6.6 Hz, 3H), 0.99 (s, 6H), 0.86 (s, 6H), 0.75 (d, J = 6.6 Hz, 1H), 0.07 (s, 9H).

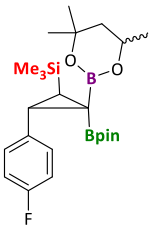
^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.1, 129.9, 113.5, 83.0, 70.9, 65.1, 55.8, 46.0, 31.7, 30.7, 30.1, 29.5, 28.6, 25.5, 24.4, 23.4, 14.6, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.4, 30.7.

HRMS (ESI) for **$C_{25}H_{42}B_2O_5Si^+[M+H^+]^+$:** calculated: 473.3054, found: 473.3056.

Melting point: 76.2 °C.

(-(3-(4-Fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)cyclopropyl)trimethylsilane (4.6)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a white solid (69%, 63 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 – 7.17 (m, 2H), 6.91 – 6.83 (m, 2H), 4.26 – 4.13 (m, 1H), 2.39 (d, J = 7.1 Hz, 1H), 1.71 (dd, J = 13.9, 3.0 Hz, 1H), 1.49 (m, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.22 (d, J = 7.2 Hz, 3H), 0.99 (s, 6H), 0.86 (s, 6H), 0.76 (d, J = 7.1 Hz, 1H), 0.07 (s, 9H).

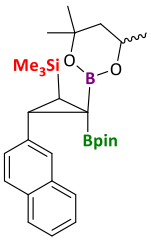
^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.7 (d, J = 242.4 Hz), 139.1 (d, J = 2.5 Hz), 130.4 (d, J = 7.7 Hz), 114.7 (d, J = 21.1 Hz), 83.1, 71.0, 65.2, 46.1, 31.8, 29.6, 28.7, 25.5, 24.5, 23.4, 14.9, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.2, 28.9.

HRMS (ESI) for **$C_{24}H_{40}B_2FO_4Si^+[M+H^+]^+$:** calculated: 461.2866, found: 461.2867.

Melting point: 78.2°C.

(3-(Naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((S)-4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)cyclopropyl)trimethylsilane (4.7)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a white solid (73%, 72 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 – 7.69 (m, 2H), 7.70 – 7.62 (m, 2H), 7.50 – 7.43 (m, 1H), 7.43 – 7.30 (m, 2H), 4.29 – 4.16 (m, 1H), 2.58 (d, J = 6.9 Hz, 1H), 1.73 (dd, J = 13.9, 3.0 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.29 (s, 3H), 1.27 (s, 3H), 1.25 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 7.4 Hz, 2H), 0.89 (s, 6H), 0.75 (s, 6H), 0.12 (s, 9H).

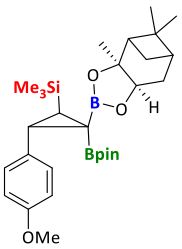
^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 133.5, 132.1, 128.2, 127.6, 127.5, 127.1, 125.6, 125.5, 124.7, 82.7, 70.7, 64.8, 45.7, 31.4, 30.3, 28.3, 25.1, 24.1, 23.1, 14.7, -0.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.5, 28.6.

HRMS (ESI) for **$C_{28}H_{43}B_2O_4Si^+[M+H^+]^+$:** calculated: 493.3117, found: 493.3121.

Melting point: 80.4 °C.

(3-(4-Methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((3aS,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)cyclopropyl)trimethylsilane (4.8)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (86%, 69 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (dd, J = 8.7, 0.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 4.26 (dd, J = 8.7, 2.0 Hz, 1H), 3.75 (s, 3H), 2.42 (d, J = 7.2 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.26 – 2.16 (m, 1H), 2.11 – 2.04 (m, 1H), 1.93 – 1.85 (m, 2H), 1.51 (d, J = 10.9 Hz, 1H), 1.37 (s, 3H), 1.30 (s, 3H), 0.98 (s, 6H), 0.86 (d, J = 7.2 Hz, 1H), 0.84 (s, 3H), 0.82 (s, 6H), 0.09 (s, 9H).

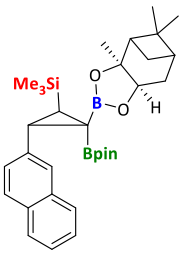
^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 134.4, 130.1, 113.1, 85.5, 82.8, 77.9, 55.5, 51.6, 39.6, 38.4, 35.5, 29.7, 28.5, 27.3, 26.2, 25.2, 24.2, 24.2, 24.2, 14.2, -0.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.6.

HRMS (ESI) for **$C_{29}H_{47}B_2O_5Si^+[M+H^+]^+$:** calculated: 525.3378, found: 525.3380.

Melting point: 80.3 °C.

(3-(Naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((3aS,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)cyclopropyl)trimethylsilane (4.9)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (94%, 88 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (m, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.53 – 7.44 (m, 1H), 7.42 – 7.33 (m, 2H), 4.29 (dd, J = 8.7, 1.9 Hz, 1H), 2.62 (d, J = 7.3 Hz, 1H), 2.38 – 2.21 (m, 2H), 2.11 (dd, J = 6.1, 4.8 Hz, 1H), 1.96 – 1.88 (m, 2H), 1.54 (d, J = 10.9 Hz, 1H), 1.40 (s, 3H), 1.31 (s, 3H), 1.08 (d, J = 7.3 Hz, 1H), 0.89 (m, 7H), 0.86 (s, 3H), 0.68 (s, 6H), 0.14 (s, 9H).

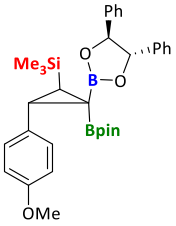
^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9, 133.4, 132.2, 128.5, 127.6, 127.5, 127.0, 126.2, 125.6, 124.9, 85.6, 82.9, 77.9, 77.4, 77.3, 77.1, 76.8, 51.6, 39.6, 38.4, 35.5, 30.7, 28.5, 27.3, 26.2, 25.1, 24.2, 14.5, -0.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.5.

HRMS (ESI) for **$C_{32}H_{47}B_2O_4Si^+[M+H^+]^+$:** calculated: 545.3429, found: 545.3432.

Melting point: 82.6 °C.

(2-((4*R*,5*S*)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)trimethylsilane (4.10)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (86%, 98 mg).

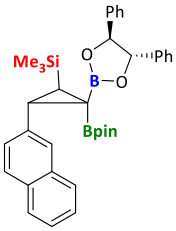
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.22 (m, 12H), 6.81 – 6.75 (m, 2H), 5.18 (s, 2H), 3.77 (s, 3H), 2.63 (d, J = 7.8 Hz, 1H), 1.04 (s, 6H), 1.03 (d, J = 7.8 Hz, 1H), 0.90 (s, 6H), 0.13 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.2, 130.0, 128.5, 128.1, 126.2, 113.1, 86.5, 83.0, 55.4, 24.9, 24.3, -1.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 28.6.

HRMS (ESI) for **$C_{33}H_{43}B_2O_5Si^+[M+H^+]^+$:** calculated: 569.3065, found: 569.3065.

(2-((4S,5R)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-3-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)trimethylsilane (4.11)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (81%, 95 mg).

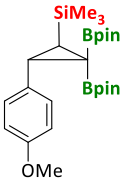
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 – 7.68 (m, 4H), 7.56 (dd, J = 8.4, 1.8 Hz, 1H), 7.41 – 7.29 (m, 11H), 6.90 (dt, J = 8.2, 7.0 Hz, 1H), 6.63 (dt, J = 8.4, 1.5 Hz, 1H), 5.23 (s, 2H), 2.90 – 2.82 (m, 1H), 0.94 (s, 6H), 0.92 – 0.81 (m, 1H), 0.76 (s, 6H), 0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.2, 129.6, 129.5, 129.3, 129.2, 129.2, 129.1, 128.5, 128.4, 128.0, 127.3, 127.2, 126.7, 126.6, 87.6, 84.0, 31.9, 25.8, 25.2, 15.6, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.5.

HRMS (ESI) for **$C_{36}H_{43}B_2O_4Si^+[M+H^+]^+$:** calculated: 588.3149, found: 588.3148.

(3-(4-Methoxyphenyl)-2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)trimethylsilane (4.12)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (100:3). The product was isolated as a pale yellowish oil (76%, 63 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 – 7.17 (m, 2H), 6.78 – 6.70 (m, 2H), 3.75 (s, 3H), 2.40 (d, J = 7.2 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 0.99 (s, 6H), 0.85 (d, J = 7.2 Hz, 1H), 0.82 (s, 6H), 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 134.4, 130.0, 113.2, 83.0, 82.8, 55.5, 29.8, 25.3, 25.1, 24.2, 14.3, -0.6.

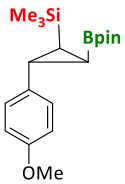
^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.2.

HRMS (ESI) for **$C_{25}H_{43}B_2O_5Si^+[M+H^+]^+$:** calculated: 473.3065, found: 473.3064.

Melting point: 76.1°C

- Characterisation data for (B, Si)-cyclopropanes

(2-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)trimethylsilane (4.13a)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish solid (80%, 55 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.77 (s, 3H), 2.07 (dd, J = 7.1, 5.9 Hz, 1H), 1.24 (s, 12H), 0.42 (dd, J = 11.5, 5.9 Hz, 1H), 0.27 (dd, J = 11.5, 7.1 Hz, 1H), 0.09 (s, 9H).

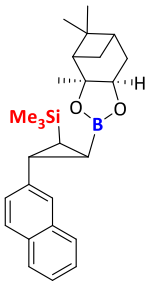
^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.7, 136.8, 126.8, 113.8, 83.2, 77.4, 77.1, 76.8, 55.4, 26.5, 25.3, 24.8, 17.1, -0.5.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.2.

HRMS (ESI) for **$C_{19}H_{32}BO_3Si^+[M+H^+]^+$:** calculated: 347.2213, found: 347.2214.

Melting point: 60.2 °C.

(2-(Naphthalen-2-yl)-3-((3aS,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)cyclopropyl)trimethylsilane (4.14)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a white solid (94%, 79 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 – 7.69 (m, 3H), 7.59 (q, J = 0.9 Hz, 1H), 7.47 – 7.33 (m, 3H), 7.19 (dd, J = 8., 1.9 Hz, 1H), 4.30 (dd, J = 8.8, 1.9 Hz, 1H), 2.37 – 2.20 (m, 3H), 2.06 (dd, J = 8.3, 3.6 Hz, 1H), 1.94 – 1.77 (m, 1H), 1.39 (s, 3H), 1.30 (s, 3H), 1.27 – 1.19 (m, 2H), 0.85 (s, 4H), 0.72 – 0.62 (m, 1H), 0.54 – 0.44 (m, 1H), 0.13 (s, 9H).

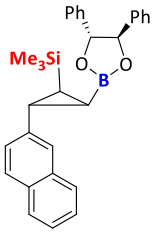
^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.8, 134.1, 132.5, 128.4, 128.1, 127.8, 126.6, 125.4, 124.7, 124.6, 86.3, 78.6, 52.0, 40.1, 38.8, 35.8, 29.2, 27.8, 27.7, 26.9, 24.6, 18.2, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.2.

HRMS (ESI) for **$C_{26}H_{35}BO_2Si^+[M+H^+]^+$:** calculated: 419.4413, found: 419.4412.

Melting point: 77.9 °C.

(2-((4R,5R)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-3-(naphthalen-2-yl)cyclopropyl)trimethylsilane (4.15)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (97%, 73 mg).

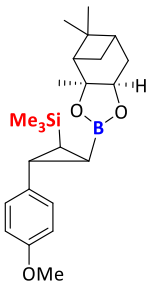
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 – 7.53 (m, 6H), 7.46 (d, J = 2.1 Hz, 2H), 7.39 – 7.20 (m, 6H), 7.08 – 6.97 (m, 2H), 6.86 (d, J = 0.8 Hz, 1H), 5.51 (s, 2H), 2.84 – 2.74 (m, 1H), 0.58 – 0.47 (m, 1H), 0.38 – 0.25 (m, 1H), -0.00 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 137.6, 128.4, 128.2, 127.8, 126.9, 126.6, 125.5, 124.8, 124.6, 83.8, 30.9, 25.9, 25.4, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.1.

HRMS (ESI) for **$C_{30}H_{31}BO_2Si^+[M+H^+]^+$:** calculated: 463.4512, found: 463.4510.

(2-(4-Methoxyphenyl)-3-((3aS,7aR)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)cyclopropyl)trimethylsilane (4.16)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (87%, 69 mg).

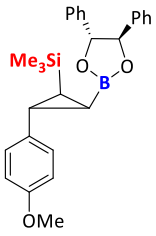
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (d, J = 8.6 Hz, 2H), 6.83 – 6.77 (m, 2H), 4.27 (dd, J = 8.6, 1.9 Hz, 1H), 3.77 (d, J = 0.7 Hz, 3H), 2.36 – 2.25 (m, 1H), 2.25 – 2.17 (m, 1H), 2.05 (dt, J = 14.4, 6.0 Hz, 2H), 1.93 – 1.82 (m, 2H), 1.36 (d, J = 0.8 Hz, 3H), 1.28 (s, 3H), 1.21 – 1.17 (m, 2H), 0.83 (s, 3H), 0.51 – 0.41 (m, 1H), 0.34 – 0.24 (m, 1H), 0.09 (s, 9H).

^{13}C NMR (CDCl3, 100 MHz) δ 157.5, 136.6, 129.8, 126.6, 113.6, 85.5, 77.8, 55.3, 51.3, 39.4, 38.1, 35.2, 30.3, 28.5, 27.0, 26.3, 26.2, 23.9, 16.8, -0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.1.

HRMS (ESI) for **$C_{23}H_{35}BO_3Si^+[M+H^+]^+$:** calculated: 399.4140, found: 399.4142.

(2-((4R,5R)-4,5-Diphenyl-1,3,2-dioxaborolan-2-yl)-3-(4-methoxyphenyl)cyclopropyl)trimethylsilane (4.17)



The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (90%, 80 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 – 7.32 (m, 5H), 7.29 (dt, J = 8.0, 2.0 Hz, 5H), 7.25 – 7.21 (m, 2H), 6.84 – 6.79 (m, 2H), 5.16 (s, 2H), 3.80 (s, 3H), 2.81 – 2.72 (m, 1H), 0.73 – 0.65 (m, 1H), 0.50 (dt, J = 9.9, 7.4 Hz, 1H), -0.20 (d, J = 1.8 Hz, 9H).

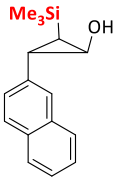
^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.6, 131.5, 129.9, 129.4, 126.8, 114.3, 87.5, 56.3, 28.3, 15.3, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 36.5.

HRMS (ESI) for **$C_{27}H_{31}BO_3SiNa^+$[M+Na]$^+$:** calculated: 465.2033, found: 465.2039.

- Characterisation data for cyclopropanol derivatives

(1S,2S,3R)-2-(naphthalen-2-yl)-3-(trimethylsilyl)cyclopropan-1-ol (4.18)



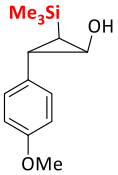
The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:1). The product was isolated as a pale yellowish oil (96%, 49 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (ddd, J = 17.8, 8.2, 1.9 Hz, 3H), 7.28 – 7.18 (m, 3H), 6.98 (dd, J = 8.5, 1.9 Hz, 1H), 3.80 (dd, J = 7.5, 2.4 Hz, 1H), 2.02 (dd, J = 8.5, 2.4 Hz, 1H), 0.86 (m, 1H), -0.01 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.1, 133.8, 132.2, 128.2, 127.9, 127.6, 126.4, 125.3, 125.1, 123.8, 60.4, 29.8, 19.8, -0.0.

Cyclopropanation reaction of transborylated alkenylboranes

2-(4-Methoxyphenyl)-3-(trimethylsilyl)cyclopropan-1-ol (4.19)



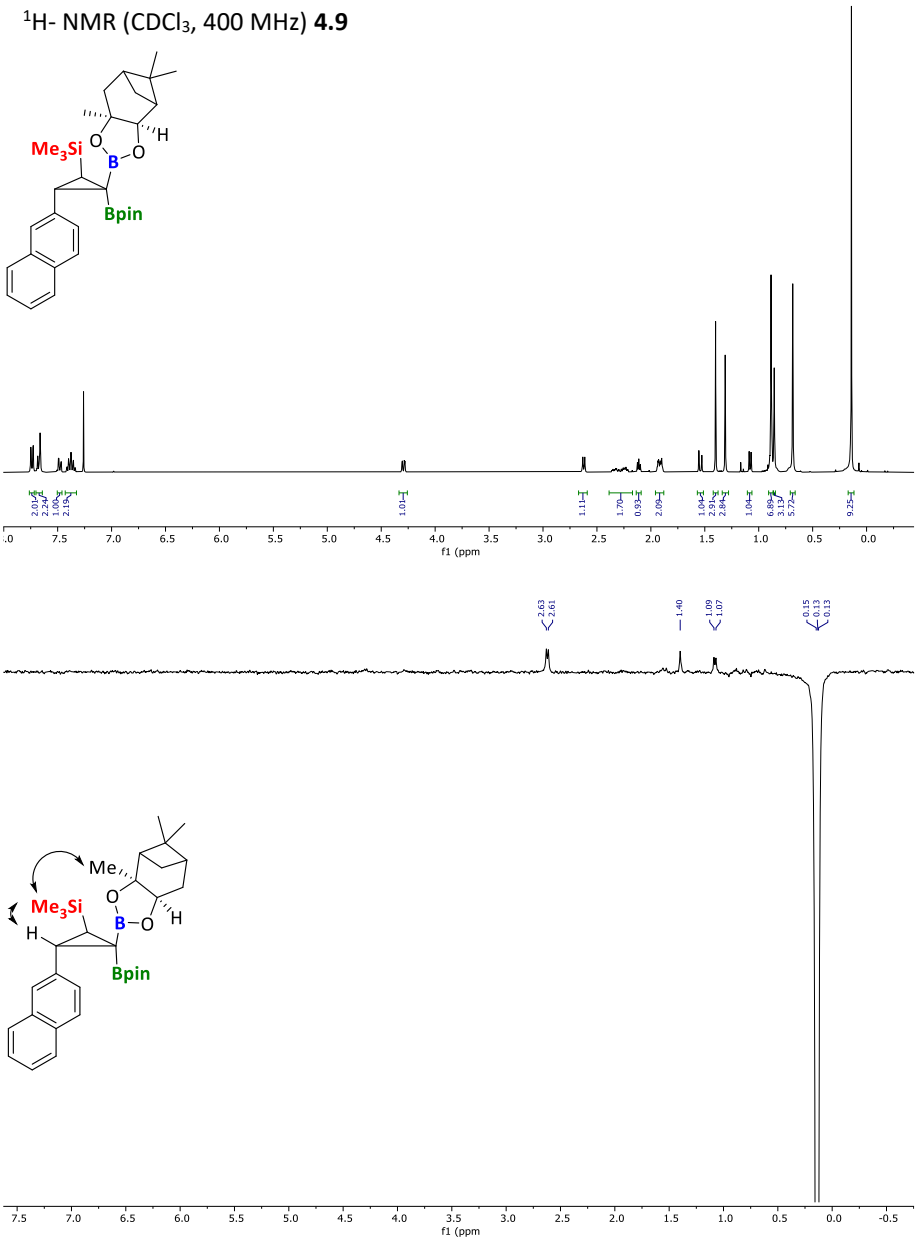
The product was purified by flash chromatography using as eluent a mixture of pentane/diethyl ether (10:2). The product was isolated as a pale yellowish oil (92%, 21 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.96 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 3.80 (dd, J = 7.4, 2.4 Hz, 1H), 3.78 (s, 3H), 2.00 (dd, J = 8.2, 2.4 Hz, 1H), 0.24 (dd, J = 8.2, 7.4 Hz, 1H), 0.13 (s, 9H).

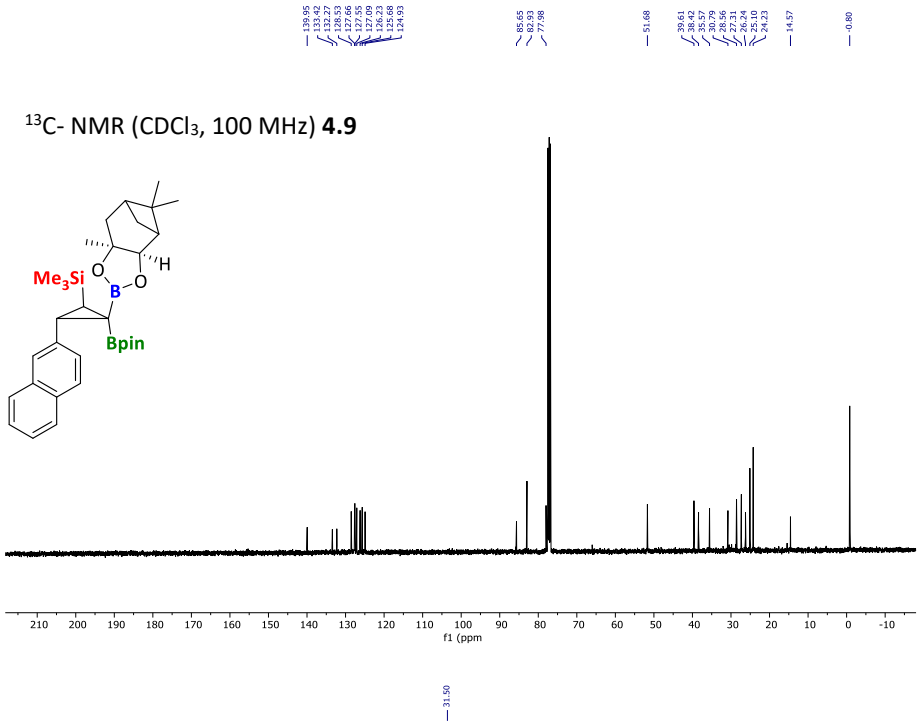
^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 134.3, 126.9, 113.9, 59.7, 55.4, 29.8, 28.5, 18.8, -0.2.

- Selected NMR spectra

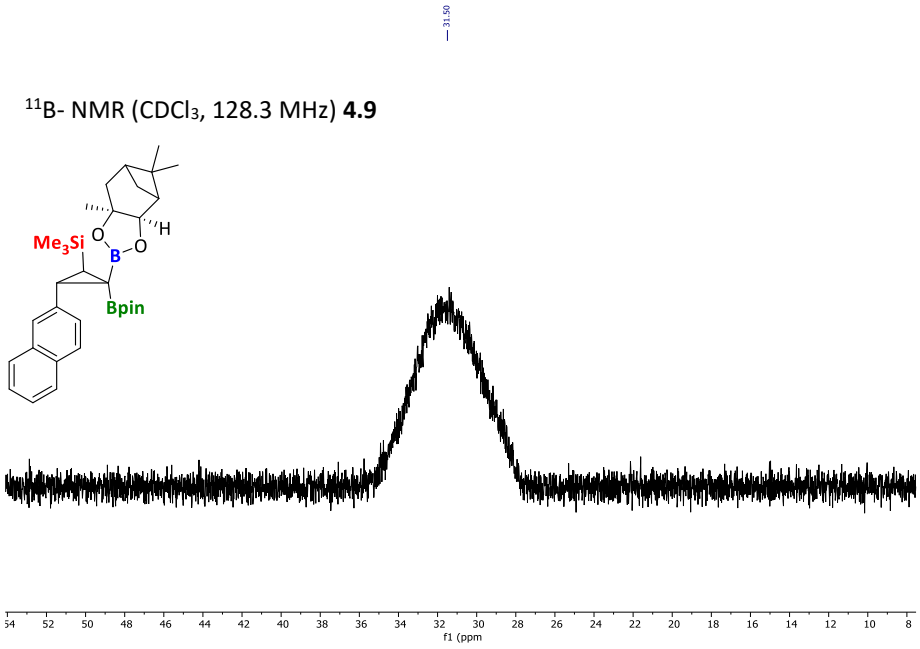
^{1}H- NMR ($CDCl_3$, 400 MHz) **4.9**



Cyclopropanation reaction of transborylated alkenylboranes

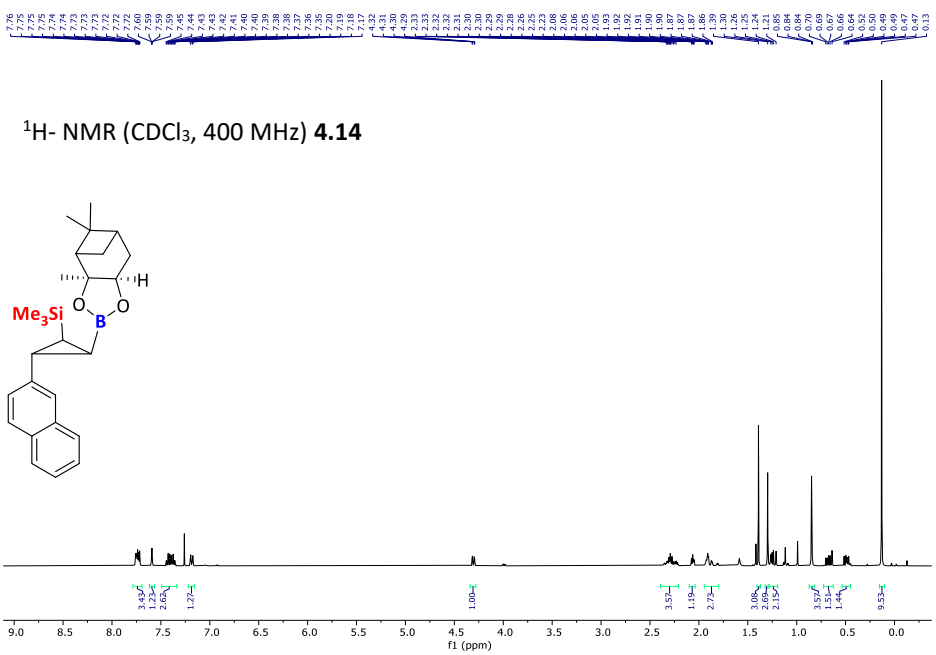


^{13}C- NMR ($CDCl_3$, 100 MHz) **4.9**

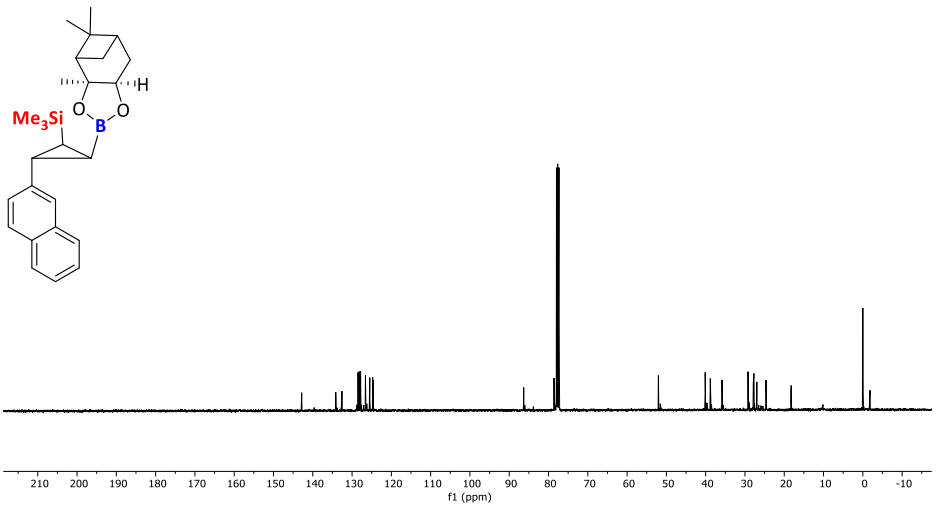


^{11}B- NMR ($CDCl_3$, 128.3 MHz) **4.9**

^{1}H- NMR ($CDCl_3$, 400 MHz) **4.14**



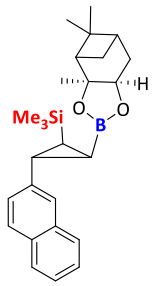
^{13}C- NMR ($CDCl_3$, 100 MHz) **4.14**

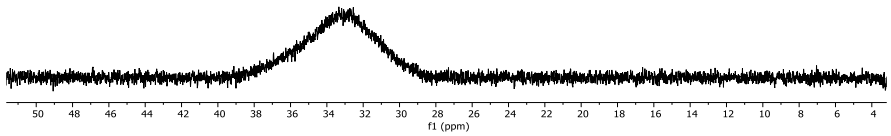


Cyclopropanation reaction of transborylated alkenylboranes

33.22

^{11}B- NMR ($CDCl_3$, 128.3 MHz) **4.14**





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UNIVERSITAT ROVIRA I VIRGILI
Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

CHAPTER V

Alkenylboranes for 1,3-boron-copper migration

UNIVERSITAT ROVIRA I VIRGILI
Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

5.1. State of the art

Catalysis with copper complexes represents one of the most powerful tools to install nucleophilic boryl units across diverse π-systems in a stereoselective manner from simple precursors.[1] These methods have established a sustainable context in catalytic reactions, enabling the exploration of the chemical space through step- and atom-economical processes.

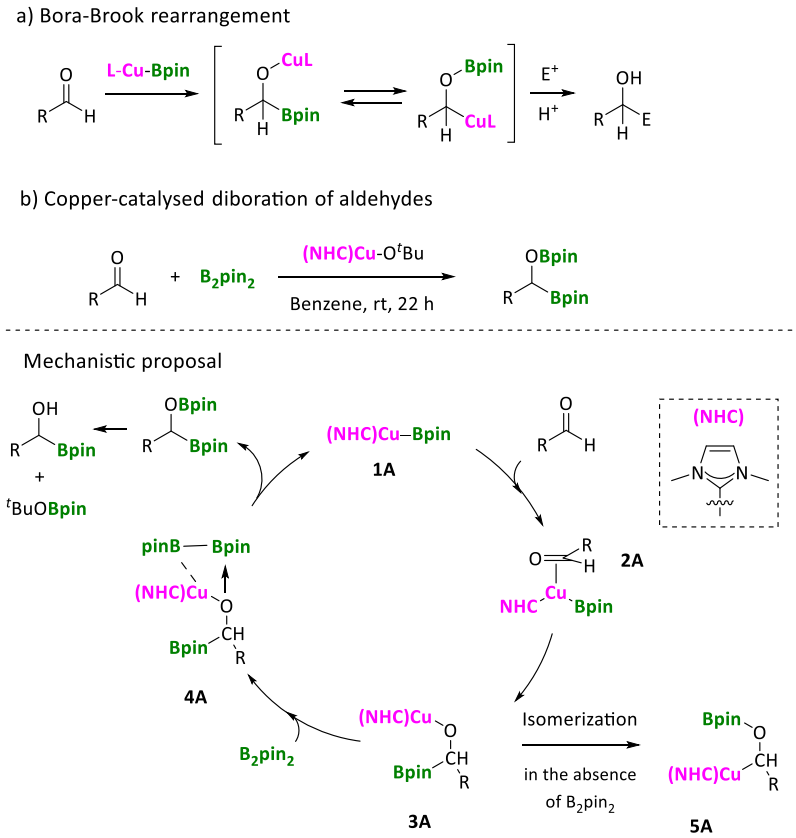
5.1.1. Acyl metalloid species into a migration strategy

By combining the diverse reactivity of carbonyls and metalloids, chemists have unlocked new opportunities to address various research challenges. Acyl metalloids represent an intriguing class of compounds because the carbonyl functional group results in an amphoteric carbon center that is nucleophilic through the carbon-metalloid σ-bond and electrophilic through its C=O π-bond.[2]

Acylboron compounds were described as fleeting intermediates due to their instability. It is well-known that the electron-deficient nature of boron encouraged nucleophiles to interact with its empty *p*-orbital. This interaction complicated traditional synthetic pathways and affected the stability of acylborane compounds, making them susceptible to oxidation or 1,2-Brook-type rearrangements.[3] This mode of reactivity was inaccessible to other acyl metalloids.

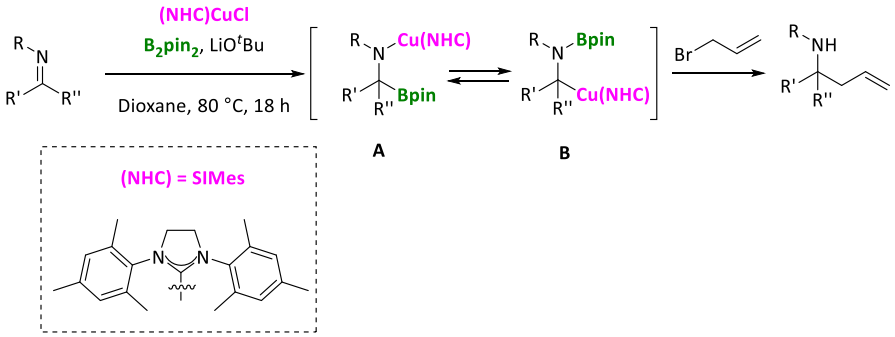
In this context, the migration of a boryl group from carbon to an adjacent oxygen atom (bora-Brook rearrangement) has been proposed to account for the observed nucleophilic reactivity of boryl-substituted alkoxide compounds towards electrophiles. Yamashita, Nozaki, and co-workers studied the ambident reactivity of the boryl-alkoxide towards electrophiles and solvents, which afforded either oxygen- or carbon-functionalised products.[4] This concept was demonstrated in the borylcupration of carbonyl compounds,[5] where the nucleophilic pinacolboryl unit (Bpin) is bonded to carbon and the Cu(I) complex to oxygen. However, an intramolecular 1,2 migration of Bpin from carbon to oxygen could occur, potentially leading to a new intermediate that may undergo electrophilic trapping at the carbon atom (Scheme 5.1a).

Alternatively, Sadighi and co-workers reported the diboration of aldehydes catalysed by *N*-heterocyclic carbene (NHC)-supported copper catalyst (Scheme 5.1b).[6a] In this context, further DFT studies on the mechanism of the reaction, conducted by Marder and Lin, revealed that the carbonyl compound was inserted into the copper-boron bond giving intermediate **3A** as the favoured kinetic species affording the Cu–O–C–B linkage (Scheme 5.1b).[6b] Subsequently, in the presence of an excess of the diboron reagent, the reaction proceeded via σ-bond metathesis giving the corresponding diborated product, which could be isolated by filtration to generate the protonated products, σ-hydroxyl alkylboronate esters. In the absence of the diboron reagent, intermediate **3A** underwent isomerisation to form the more thermodynamically stable Cu–C–O–B isomer. This transformation occurred via 1,2-boryl migration.



Scheme 5.1. Mechanistic proposal for a) the bora-Brook rearrangement and b) the copper-catalysed diboration of carbonyl compounds.

More recently, a similar rearrangement has been identified in the copper-catalysed of imines, studied by Hou, Zhang, and co-workers.[7] They have developed a selective formation of homoallylamines in the presence of a copper catalyst, B_2pin_2, and LiO^tBu. This occurred through the nucleophilic addition of a borylcopper species to the double bond of an imine generating the α-borylalkylamido copper intermediates (**A**). The subsequent 1,2-migration of a pinacolboryl group from carbon to nitrogen, accompanied by copper migration from nitrogen to carbon would afford an α-borylaminoalkyl copper species (**B**), that might evolve to the corresponding *N*-borylated homoallylamine product by the electrophilic trapping of allyl bromide at the carbon atom. Finally, the *N*-borylated homoallylamine was converted into the corresponding amine after protonolysis (Scheme 5.2).

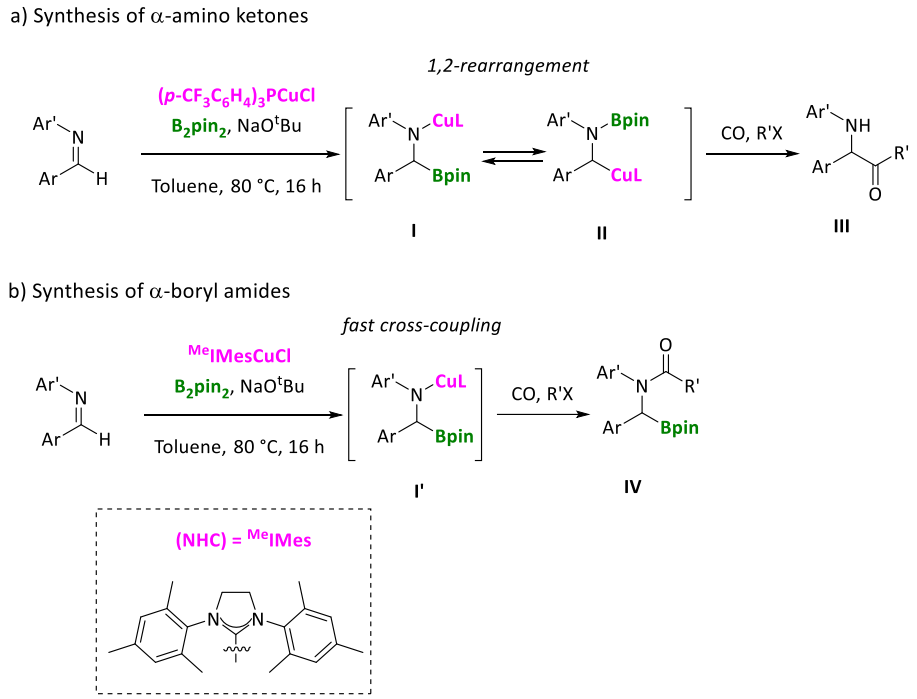


Scheme 5.2. Catalytic allylation of imines.

Additionally, Wu and co-workers developed a copper-catalysed regiodivergent borocarbonylation of imines with alkyl iodides.[8] The choice of ligand was crucial for controlling regioselectivity: using P(*p*-$CF_3C_6H_4)_3$ as the ligand resulted in the selective production of σ-amino ketones in good yields, whereas the corresponding σ-boryl amides were obtained in high regioselectivity when using the *N*-heterocyclic ligand ^{Me}IMes (Scheme 5.3).

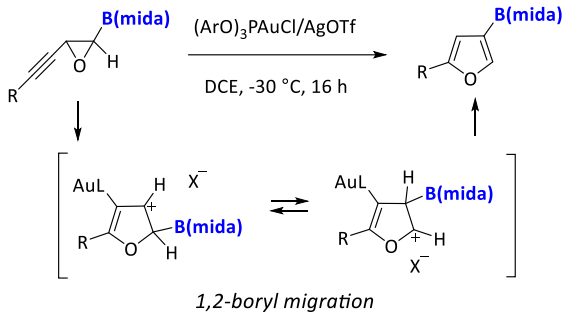
In the presence of electron-deficient ligands, the N–Cu(L) bond is weaker, and the copper species **I** followed an intramolecular 1,2-rearrangement to afford α-amino alkylcopper complex **II** that evolved towards α-amino ketones **III** by reaction with CO and R'X in MeOH (Scheme 5.3). On the other hand, under the assistance of the electron-releasing ^{Me}IMes ligand, the cross-coupling reaction between electron-rich

intermediate copper complex **I'** promoted a fast cross-coupling with CO and R'X to yield α-boryl amides **IV**. The presence of neighbouring heteroatoms (O, N) was believed to enhance the migratory aptitude of Bpin moieties due to a balance between bond energy values and the relative stability of the resulting carbanions.



Scheme 5.3. Proposed intermediates for the a) synthesis of α-amino ketones **III** and b) synthesis of α-boryl amides **IV.**

The more stable (less Lewis Acid) boryl group Bmida (mida= *N*-methyliminodiacetic acid) has also experimented boryl migration sequences through 1,2-shifts, with Cu or Au complexes, as reported by Gevorgyan and co-workers.[9] Depending on the choice of ligand and counterion, regioisomeric boryl furans could be selectively obtained by favouring the 1,2-boryl migration (Scheme 5.4). Thus, the phosphite gold complex with a triflate counterion strongly favoured a 1,2-boryl migration during the cycloisomerisation process, resulting in the formation of C_3-borylated furans. In contrast, using NHC gold hexafluoroantimonate exclusively yielded C_2-borylated furans.



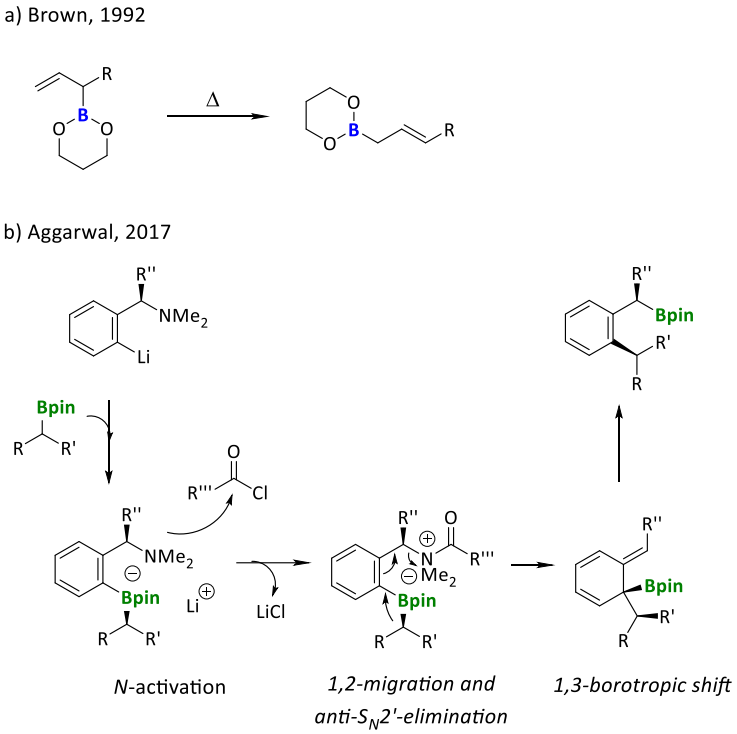
Scheme 5.4. Proposed intermediates for the gold-catalysed cycloisomerisation by 1,2-boryl migration.

5.1.2. 1,3-Boron shift-type of allylboronic and homoallenylboronic esters

Rearrangement reactions of boron compounds have demonstrated versatile reactivities for the skeleton reconstruction of more complex molecular frameworks. In this context, a series of 1,3-boryl migrations of allylboronic and homoallenylboronic esters have been reported by different groups.

The first example of a 1,3-boron shift of allylboronic ester under thermal conditions was reported by Brown and co-workers in 1992 (Scheme 5.5a).[10] σ-Vinylboronate esters were readily isomerised, under thermal conditions, affording the corresponding allylboronate esters with the boron atom on the less substituted carbon atom.

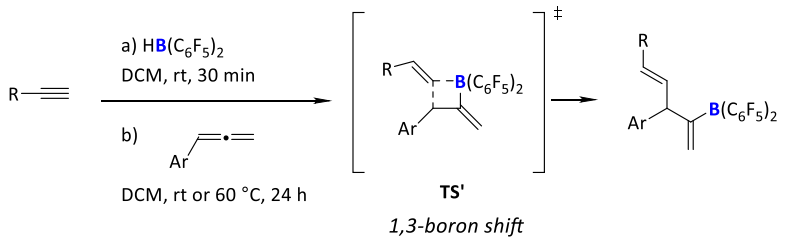
Similarly, Aggarwal and co-workers studied a stereospecific coupling between *ortho*-lithiated benzylamines with boronic esters (Scheme 5.5b).[11] The method relied on *N*-activation of the boronate complex, which underwent a 1,2-metalate rearrangement/anti-S_N2' reaction of the carbamate to form a dearomatised intermediate. This was followed by a suprafacial 1,3-borotropic shift, yielding the desired aromatic product. This sequence produced sp^2–sp^3 cross-coupled products with high enantiopurity, retaining the Bpin moiety for subsequent transformations.



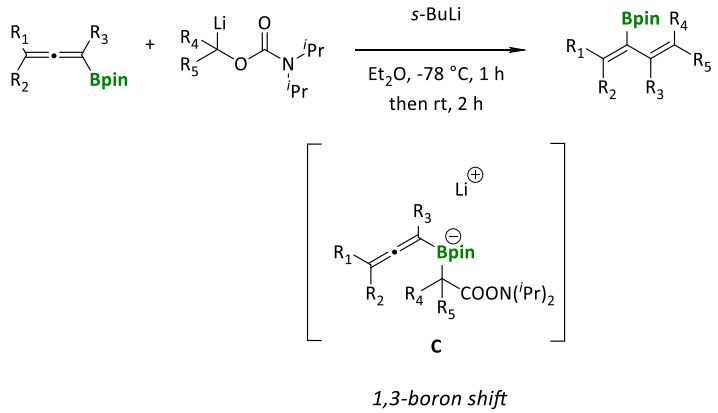
Scheme 5.5. 1,3-Boron shift of allylboronic esters.

In 2022, Gellrich and co-workers described the 1,2-carboboration of arylallenes by alkenylboranes for the synthesis of 1,4-dienes (Scheme 5.6a).[12] Notably, the mechanism of the reaction was examined. They considered that hydroboration of the substrate would occur to form the alkenylborane, which reacted with the arylallene affording the zwitterion intermediate species. In this step, they considered the formation of a transition state (**TS'**) suggesting a 1,3-boron shift mechanism, promoting the formation of the corresponding 1,4-diene. On the other hand, a 1,3-boron shift reaction of allenylboronic esters has also been reported by Nagasawa and co-workers (Scheme 5.6b).[13] Mechanistically, it has been suggested the generation of the boronate complex **C** that underwent a 1,3-boron shift reaction to generate the corresponding boryldiene product.

a) Gellrich, 2022



b) Nagasawa, 2023



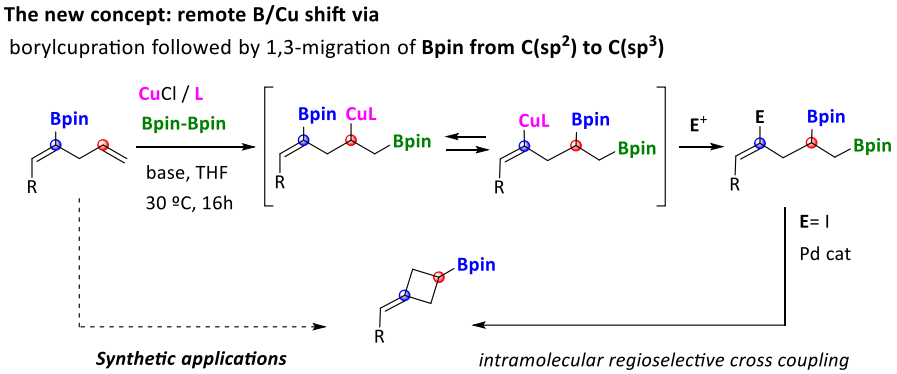
Scheme 5.6. Examples of 1,3-boron shifts towards boryldiene products.

5.2. Project aims

Here, we envisioned a novel B/Cu shift from remote C(sp^2)–Bpin and C(sp^3)–Cu units generated through the borylcupration of borylated skipped (*Z*)-dienes (Scheme 5.7).

The specific objectives are:

- Study of a new carbon-to-carbon boryl migration.
- Understanding of the stereospecifity around the alkene and in situ stereoselective electrophilic trapping.
- Synthetic application of the novel diborated products, through a palladium-catalysed regioselective intramolecular coupling to prepare functionalised alkylidenecyclobutanes.

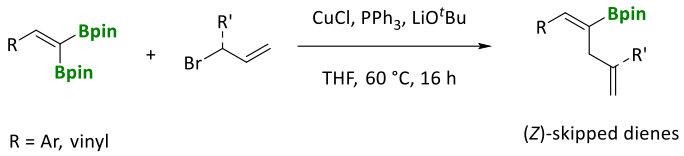


Scheme 5.7. Proposed objectives for the project.

5.3. Results and discussion

5.3.1. Optimisation studies of boron-copper 1,3-rearrangement

To illustrate this concept, we first prepared a range of borylated skipped (*Z*)-dienes using a methodology previously described by our group.[14] These were efficiently synthesised from *gem*-diborylalkenes through a site-selective activation employing a copper-catalysed system (Scheme 5.8). Moreover, this methodology was applicable to 2-substituted aryl and vinyl 1,1-diborylalkenes, enabling efficient coupling with different types of allyl halides.



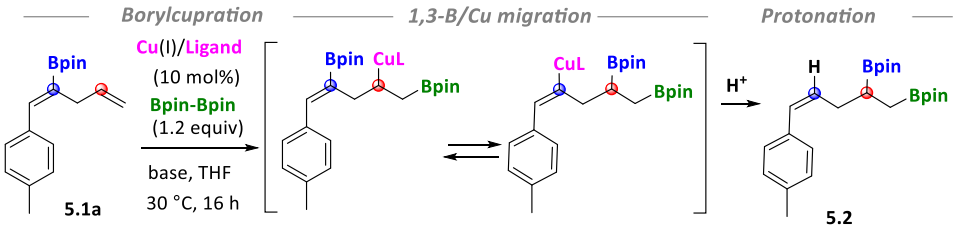
Scheme 5.8. Cu(I)-phosphine catalytic system to synthesise (*Z*)-skipped dienes.

To search for the viability of our work hypothesis, we selected the model substrate (*Z*)-2-pinacolboryl 1-(p-tolyl)penta-1,4-diene (**5.1a**) to carry out the optimisation studies. We initially explored the influence of Cu salts, ligands, and bases for the borylcupration reaction. From the diverse array of potential copper(I) catalytic systems that perform borylcupration sequences, we selected the CuCl/Xantphos catalyst, inspired by Ito's work on regioselective borylcupration[15,16] and our group experience.[17,18]

The conversion of **5.1a** into diborated alkene **5.2** was quantitatively performed with 10 mol% of CuCl/Xantphos, in the presence of 1.2 equivalents of B_2pin_2 and KO^{t}Bu as the base, at 30 °C in THF (Table 5.1, entry 1). Alternatively, using $[Cu(MeCN)_4]PF_6$ instead of CuCl, also yielded **5.2** in a similar quantitative yield (Table 5.1, entry 2). The nature of the base notably influenced the reaction outcome, since KO^{t}Bu or LiO^{t}Bu provided similar high transformations of **5.1a** into **5.2**, whereas KOMe appeared to inhibit the borylcupration of **5.1a** (Table 5.1, entries 1, 3, 4). It is worth mentioning that the site-selective activation of *gem*-diborylalkenes with Cu(I) to synthesise borylated (*Z*)-skipped dienes of type **5.1a** has also been reported to be inhibited by the presence of KOMe.[14] The use of alternative phosphines was considered for the

optimisation reaction. Replacing Xantphos with other diphosphines, such as 1,3-bis(diphenylphosphino)propane (dppp) or monophosphines (PPh_3, PCy_3), resulted in less efficient or inhibited transformations (Table 5.1, entry 5). The conversions were calculated from ^1H NMR spectra using naphthalene as an internal standard.

Table 5.1 Optimisation of the reaction conditions for the borylcupration of **5.1a** with subsequent 1,3-B/Cu migration and protonation reactions.[a]



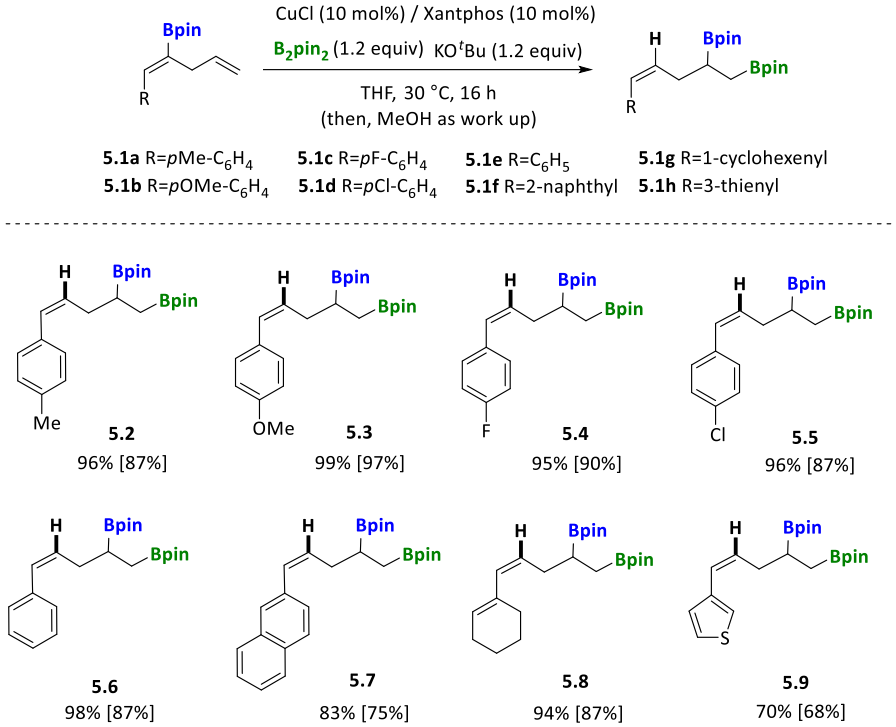
ENTRY	CU(I)	LIGAND	BASE	YIELD 5.2[b] (%)
1	CuCl	Xantphos	KO^{t}Bu	96% [87%]
2	$[Cu(MeCN)_4]PF_6$	Xantphos	KO^{t}Bu	97%
3	CuCl	Xantphos	LiO^{t}Bu	98%
4	CuCl	Xantphos	KOMe	0
5	CuCl	PPh_3	KO^{t}Bu	0

[a]Reactions were performed with 0.2 mmol of the model substrate **5.1a**, B_2pin_2 (1.2 equiv), Cu(I) source (10 mol%), ligand= Xantphos (10 mol%) or PPh_3 (20 mol%), and 1.2 equivalents of the base in 2 mL of THF as solvent at 30 °C in 16 h. [b]Yields were calculated from ^1H-NMR using naphthalene as an internal standard. Isolated yields in brackets.

A preliminary understanding of the diborated product **5.2** generated from **5.1**, suggested that the borylcupration might took place in a regioselective manner to generate the first intermediate, which further evolved the second intermediate via 1,3-boryl migration that was eventually protonated to deliver the diborated product **5.2**.

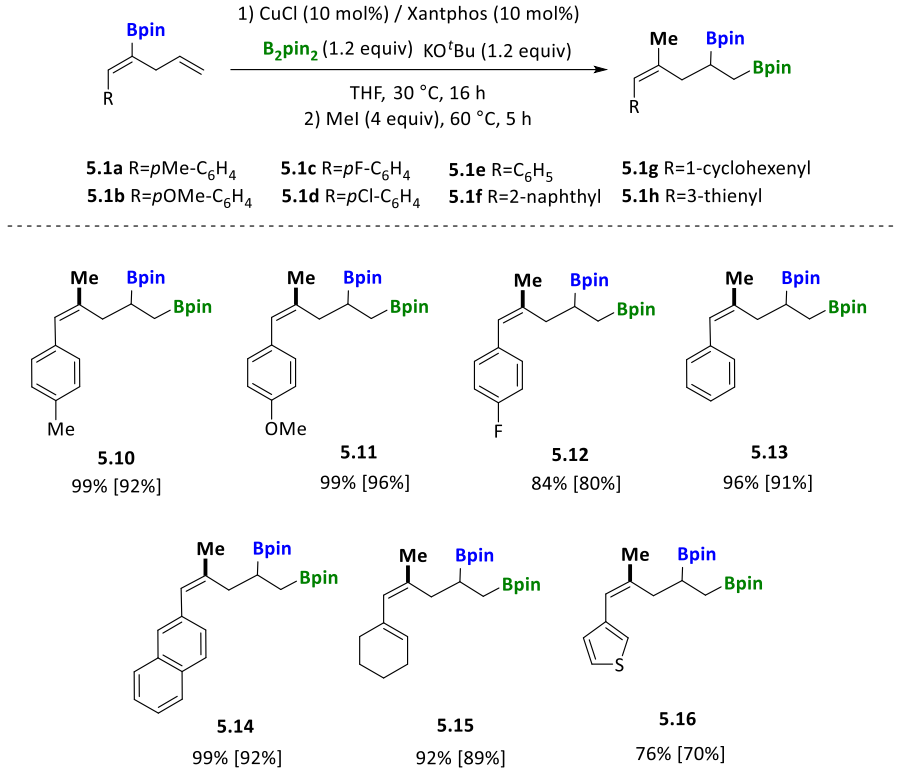
5.3.2. Substrate scope of boron-copper 1,3-rearrangement

With the optimised reaction conditions for sequential selective borylcupration, 1,3-B/Cu shift, and protonation in a single operation, we explored the compatibility of aryl groups containing electron-donating and electron-withdrawing substituents (Scheme 5.9). Generally, substrates were successfully transformed into the desired products **5.2**-**5.6**, regardless of the electronic properties of the aryl group. Additionally, the aryl group 2-naphthyl was compatible with the intramolecular 1,3-B/Cu shift, yielding the expected product **5.7** in high yield. The borylated skipped (*Z*)-dienes **5.1g** and **5.1h**, containing 1-cyclohexenyl and 3-thienyl groups respectively, underwent chemoselective copper-catalysed borylcupration at the terminal double bond, followed by stereospecific 1,3-B/Cu shift. This process generated the polyolefinic diborated compounds **5.8** and **5.9**, demonstrating the reaction's compatibility with other unsaturated functional groups.



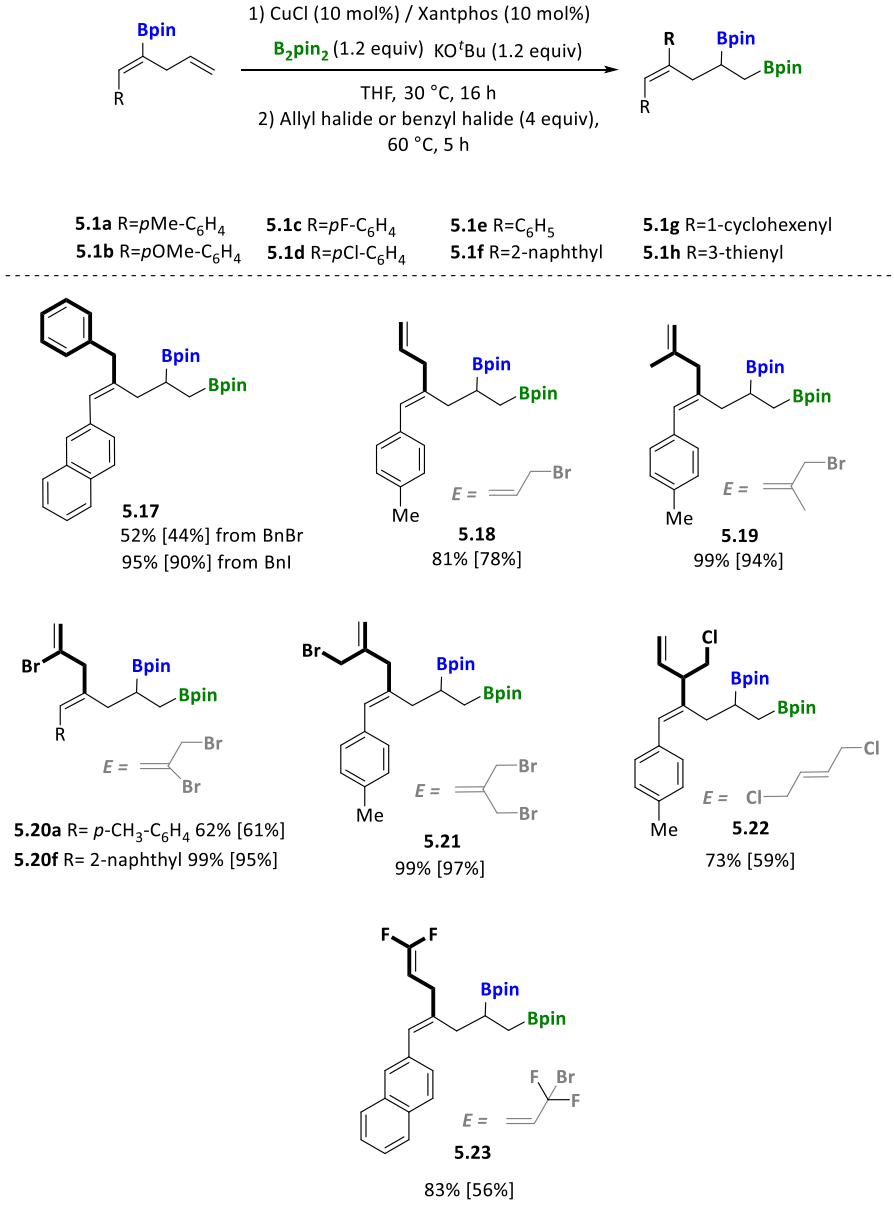
Scheme 5.9. Substrate scope for the 1,3-boron/copper rearrangement followed by protonation reaction. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

Inspired by these results, we explored the one-pot borylcupration of **5.1a**-**5.1h**, followed by a 1,3-B/Cu shift and stereospecific C–C coupling with MeI at 60 °C for 5 hours (Scheme 5.10). To our delight, the methylated products were isolated in high yields and characterised as stereoselective trisubstituted alkenes **5.10**-**5.16** (Scheme 5.10).



Scheme 5.10. Substrate scope for the 1,3-boron/copper rearrangement followed by electrophilic trapping of MeI. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

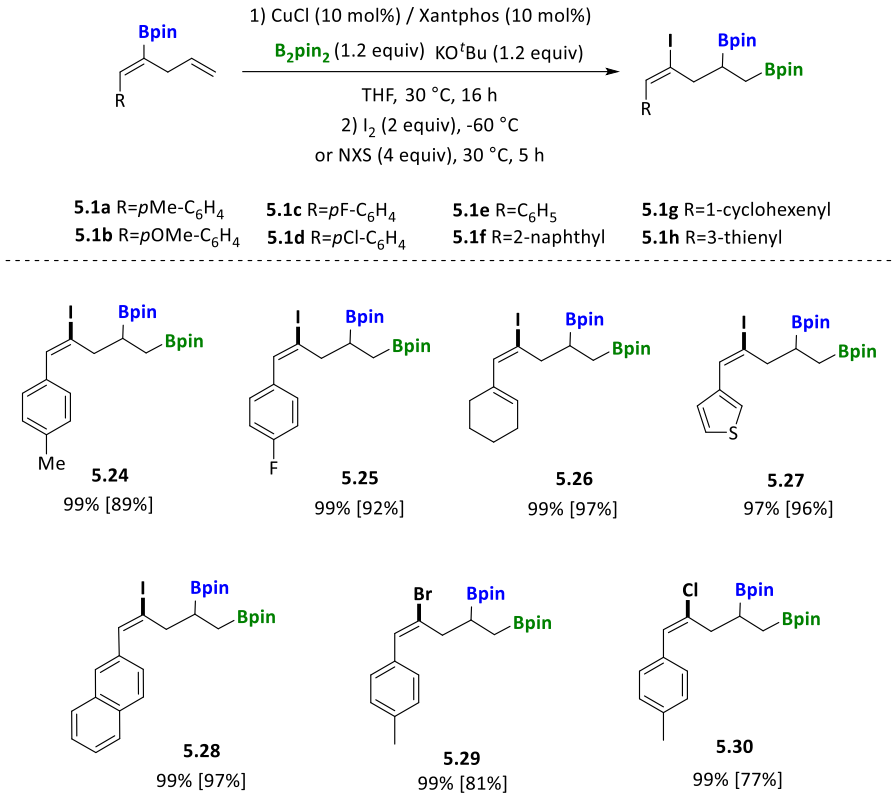
The stereospecific coupling was extended to benzyl halides, transforming **5.1f** into compound **5.17** through a reaction with BnBr or BnI, proving that BnI resulted more reactive, as expected (Scheme 5.11). However, electrophilic trapping was unproductive for secondary or tertiary alkyl halides, suggesting that the Cu–C(sp^2) nucleophilic reaction might occur via an S_N2 mechanism. When terminal and internal allyl halides were used as electrophilic partners, we observed the efficient transformation of **5.1a** or **5.1f** into products **5.18**-**5.22**, with moderate to high yields depending on the steric hindrance of the allyl bromide (Scheme 5.11). Reactivity with 3-bromo-3,3-difluoroprop-1-ene converted **5.1f** into perfluorinated alkene system **5.23**, in high yield (Scheme 5.11). Based on the reaction outcomes, the C–C coupling might proceed through S_N2' mechanism.



Scheme 5.11. Substrate scope for the 1,3-boron/copper rearrangement followed by electrophilic trapping of allyl halides. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

Additionally, we conducted the I_2-iodonolysis[19] of the alkenyl copper (I) intermediates generated after borylcupration and 1,3-B/Cu shift, producing key vinylic iodide products **5.24**-**5.28** in high yields (Scheme 5.12). Alternatively, brominated and chlorinated trisubstituted alkenes **5.29** and **5.30** were efficiently generated through

stereospecific electrophilic trapping by adding NBS or NCS, respectively (Scheme 5.12).



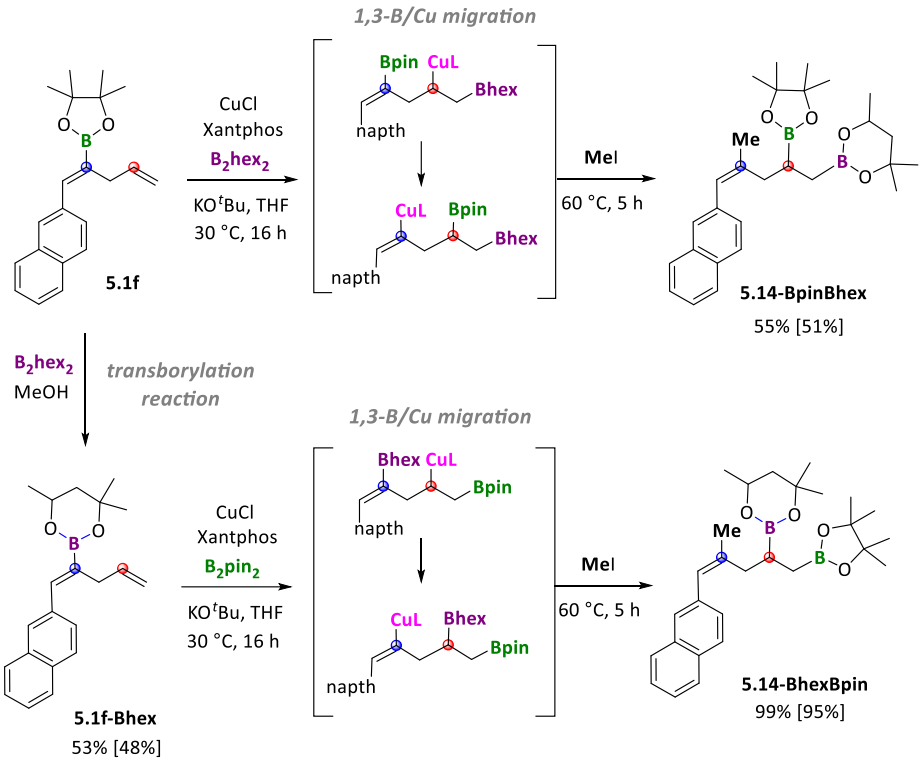
Scheme 5.12. Substrate scope for the 1,3-boron/copper rearrangement followed by electrophilic trapping of I_2 or NXS. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields are shown in brackets.

5.3.3. Study about stereoselectivity on 1,3-boron/copper shift

We have pursued the formation of regioselective mixed diborated products through two complementary strategies. Initially, when substrate **5.1f** reacted with bis(hexylene glycolato)diboron (B_2hex_2), in the presence of CuCl/Xantphos catalytic system, the borylcupration reaction occurred, placing the Bhex moiety at the terminal position of the double bond that followed a subsequent 1,3-Bpin/Cu shift. Eventually, the electrophilic coupling with MeI, generated the mixed product **5.14-BpinBhex** in 51% isolated yield (Scheme 5.13). In parallel, we transborylated **5.1f** into **5.1f-hex** via a convenient C(sp^2)–Bpin / B_2hex_2 cross-metathesis,[20] aiming to conduct the

borylcupration of **5.1f-hex** with B_2pin_2. This was followed by a catalytic system 1,3-Bhex/Cu shift with subsequent coupling with MeI, generating the mixed alkene **5.14-BhexBpin** in 95% isolated yield, with the Bhex moiety at internal position (Scheme 5.13).

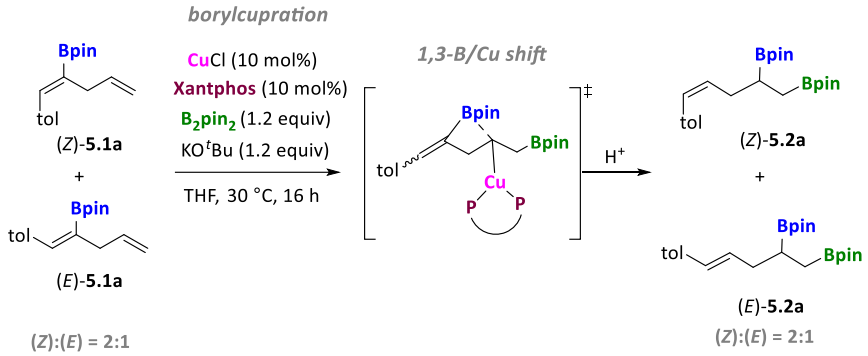
These experiments demonstrated that the 1,3-B/Cu shift was compatible with different boryl moieties other than pinacolboryl moiety, allowing the synthesis and isolation of both regioisomers, **5.14-BpinBhex** and **5.14-BhexBpin**.



Scheme 5.13. 1,3-B/Cu shift with mixed boryl systems and electrophilic trapping with MeI. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields in brackets.

On the other hand, to gain a comprehensive understanding of the mechanism, we conducted an experiment involving both stereoisomers of the borylated skipped diene **5.1a** as a mixture of (*Z*):(*E*) 2:1 (Scheme 5.14). This mixture underwent a *one-pot* borylcupration followed by 1,3-B/Cu shift and protonation, resulting in the formation of (*Z*)-**5.2** and (*E*)-**5.2** in the same 2:1 ratio. The reaction outcome indicated that both

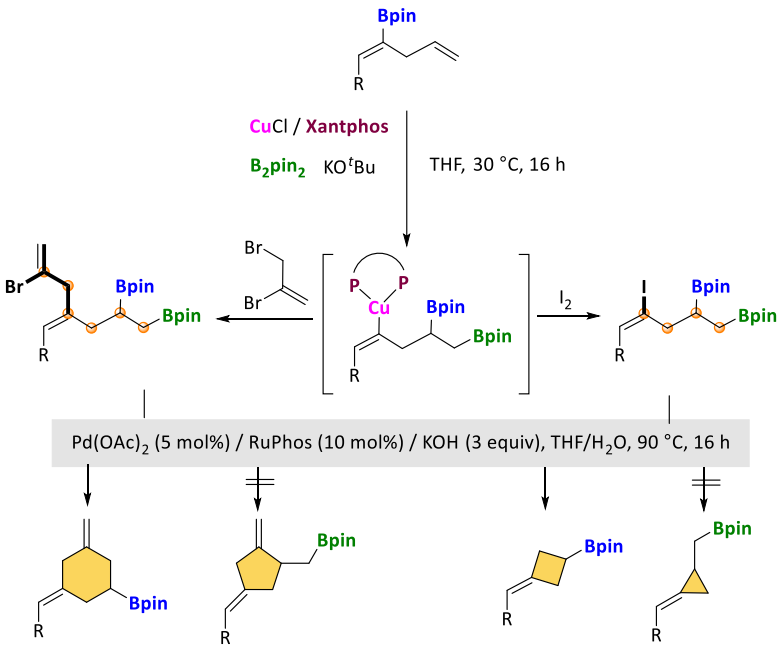
isomers proceeded with a similar energetic profile, besides the relative positions of the aryl group on the skipped diene substrate.



Scheme 5.14. Borylcupration of (*Z*)-**5.1a**:(*E*)-**5.1a** = 2:1 followed by 1,3-B/Cu shift – protonation.

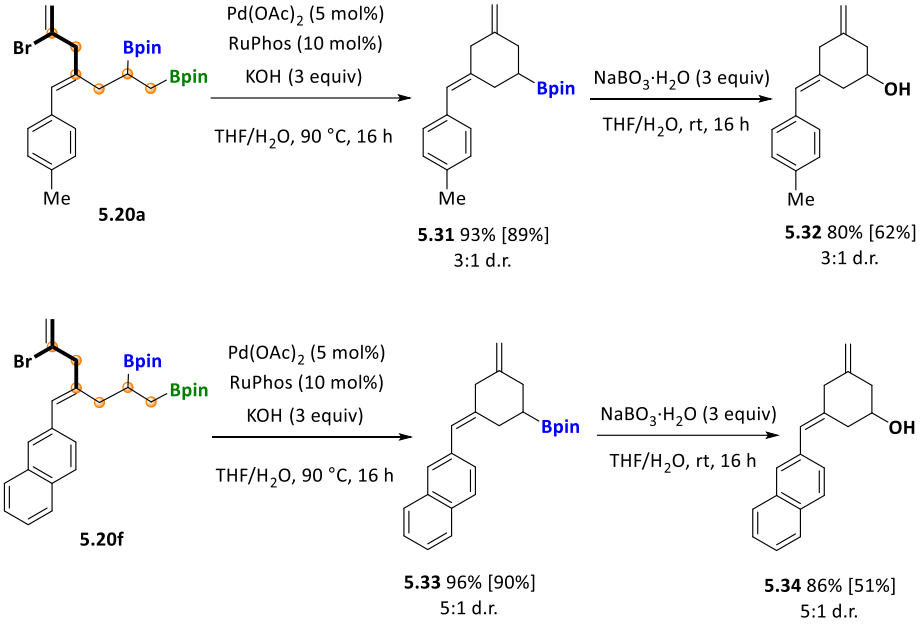
5.3.4. Synthetic applications via palladium-catalysed cross-coupling reaction

All the polyfunctionalised alkenes synthesised in this work (**5.2**-**5.30**) have been synthesised for the first time, and we proved their potential for synthetic applications. palladium-catalysed cross-coupling could transform them into functionalised alkylidenecycloalkanes with six-, five-, four-, or three-membered rings (Scheme 5.15).



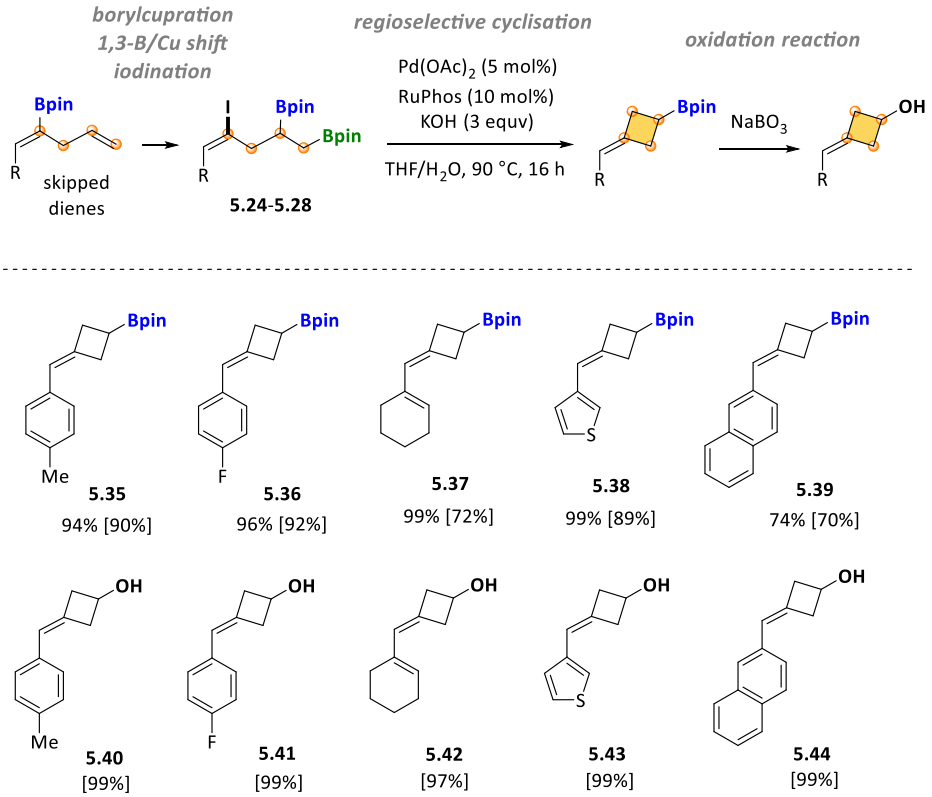
Scheme 5.15. Potential synthetic application throughout Pd-catalysed cross-coupling to be converted into functionalised alkylidenecycloalkanes.

We were pleased to find that when the polyfunctionalised skipped compound **5.20a** reacted with $Pd(OAc)_2$/Ruphos,[21] underwent a regioselective cyclisation with the terminal Bpin moiety, forming exclusively the six-membered ring product **5.31**, that contained two exocyclic alkene motifs and retained the original Bpin moiety from the starting material **5.1a** (Scheme 5.16). The alkylidenecyclohexane **5.31** was isolated as a 3:1 stereoisomeric mixture, and subsequent oxidation yielded the corresponding secondary alcohol **5.32**. In the case of the more sterically hindered polyfunctionalised skipped compound **5.20f**, palladium-catalysed cyclisation produced alkylidenecyclohexane **5.33** in high yield with an increased diastereomeric ratio (up to 5:1), which was also observed in the corresponding alcohol **5.34** (Scheme 5.16).



Scheme 5.16. Regioselective palladium-cyclisation towards alkylidenecyclohexane synthesis and oxidation to vinylidenecyclohexanols. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields in brackets.

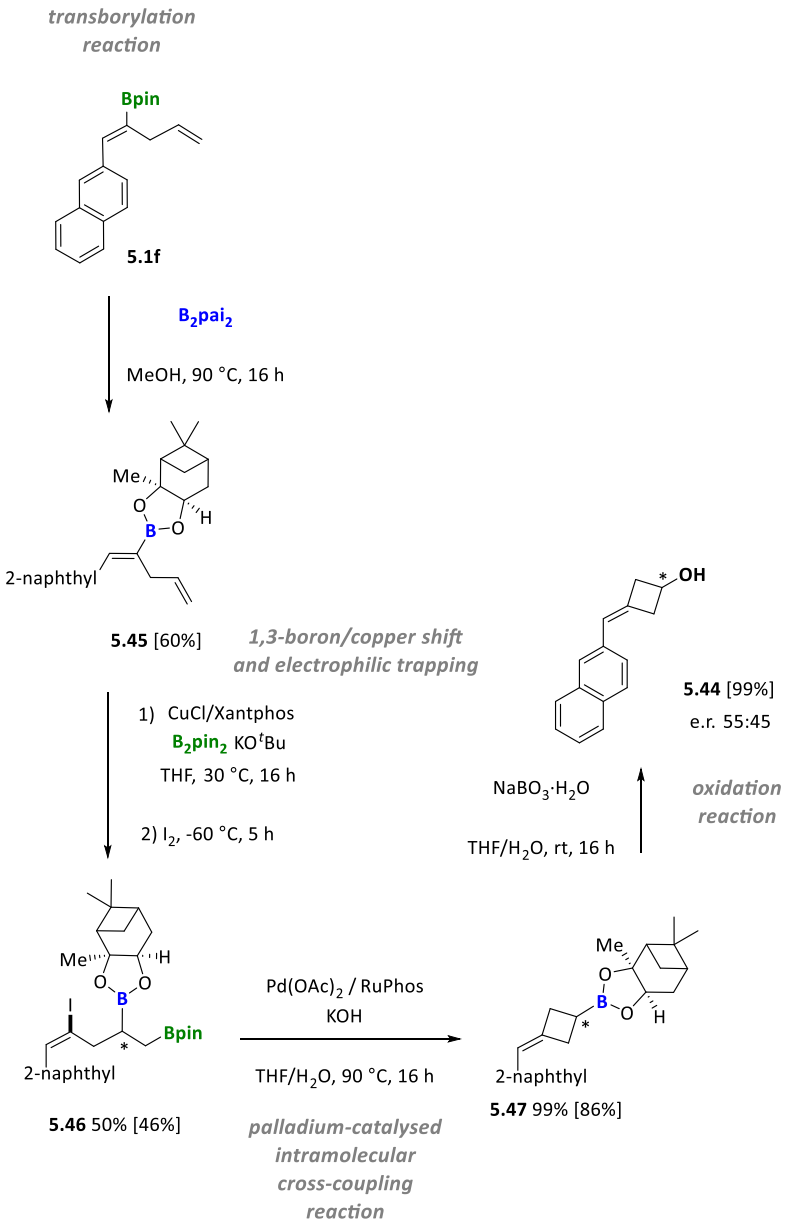
Similarly, the Pd-catalysed cyclisation of (*E*)-iodo substituted alkene **5.24** resulted in the exclusive formation of alkylidenecyclobutane **5.35**, a particular class of highly strained yet stable molecules (Scheme 5.17). Given that these compounds have recently proven to be valuable structural motifs in various natural products[22] and versatile intermediates in organic synthesis,[23] we aim to generalise this Pd-catalysed cyclisation to (*E*)-iodo substituted alkenes **5.24**-**5.28**. Upon conducting these reactions, we observed a consistent trend in synthesising the four-membered rings **5.35**-**5.39** in high yields (Scheme 5.17). These transformations were tolerant with both electron-donating and electron-withdrawing aryl or vinyl groups in the substrates. Oxidation of the C–Bpin bonds in the exobutanocyclic alkenes yielded aryl- or vinylidene cyclobutanols **5.40**-**5.44** quantitatively, contributing to the first synthesis of these compounds, to the best of our knowledge (Scheme 5.17).



Scheme 5.17. Regioselective Pd-cyclisation towards alkylidenecyclobutane synthesis and oxidation to vinylidene cyclobutanols. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields in brackets.

5.3.5. Attempts towards the asymmetric version of 1,3-boryl migration reaction

We attempted to perform the asymmetric version of 1,3-boron/copper shift by an asymmetric induction of the (+)-pinanediolboryl moiety (Bpai) (Scheme 5.18). In this context, the transborylated product **5.45** was synthesised by a transborylation reaction of substrate **5.1f** with chiral diboron reagent B_2pai_2. Next, it was performed the consecutive borylcupration – 1,3-B/Cu shift – iodination reaction to give the mixed boryl compound **5.46** in moderate yield. Throughout the palladium-cyclisation and the subsequent oxidation, we were able to obtain product **5.44**, although with a scare 55:45 enantiomeric ratio. This was likely caused by the distance between the chiral boryl group, which holds the asymmetric information, and the position where the 1,3-boron/copper shift occurs.



Scheme 5.18. Asymmetric version through chiral Bpai transborylation. Yields determined by NMR spectroscopy with naphthalene as internal standard. Isolated yields in brackets.

5.4. Computational studies (carried out by Prof. Carbó)

DFT calculations were performed by Dr. Ricardo J. Maza and Prof. Jorge J. Carbó to elucidate the reaction mechanism of the stereospecific borylcupration – 1,3-B/Cu shift – methylation of borylated skipped (*Z*)-dienes, as well as to understand the role of the base on the catalytic activity.[24]

As demonstrated in previous computational studies,[18] **I1** underwent σ-bond metathesis with B_2pin_2 to form the Cu(I)-boryl species (**I2**), a process that was thermodynamically favorable by 17.7 kcal·mol^{-1} (Figure 5.1). In the next step, substrate **5.1a** coordinated with the Cu complex via the terminal double bond, forming the **I3** adduct. The subsequent regioselective insertion of the C=C double bond into the Cu–B bond produced the alkyl–copper(I) complex **I4**, with the Bpin moiety attached to the terminal carbon. It is important to note that our experiments have demonstrated that borylcupration was chemoselective for the terminal double bond, even in the presence of internal or endocyclic alkene moieties.

From intermediate **I4**, the intramolecular B/Cu 1,3-rearrangement involved the migration of the Bpin moiety from C(sp^2) to C(sp^3) in two steps (Figure 5.1). First, the nucleophilic attack of the copper-alkyl moiety on the boron atom bonded to the C(sp^2) forms a 4-membered boracycle structure, which remained bonded to copper through an oxygen atom of the pinacol group (intermediate **I5**). Next, the copper migrated to the C(sp^2), accompanied by the ring opening of the B–C(sp^2) bond, resulting in the alkenyl copper intermediate **I6**. Finally, the base KO^{t}Bu could transmetallate with the Cu-alkenyl complex **I6**, forming the 5-membered boracycle compound **I7**, which was stabilised by the K^+ countercation. This process potentially regenerated the Cu–O^{t}Bu catalytic system **I1**. The overall 1,3-B/Cu shift process had a moderate computed free-energy barrier of 19.4 kcal·mol^{-1}.

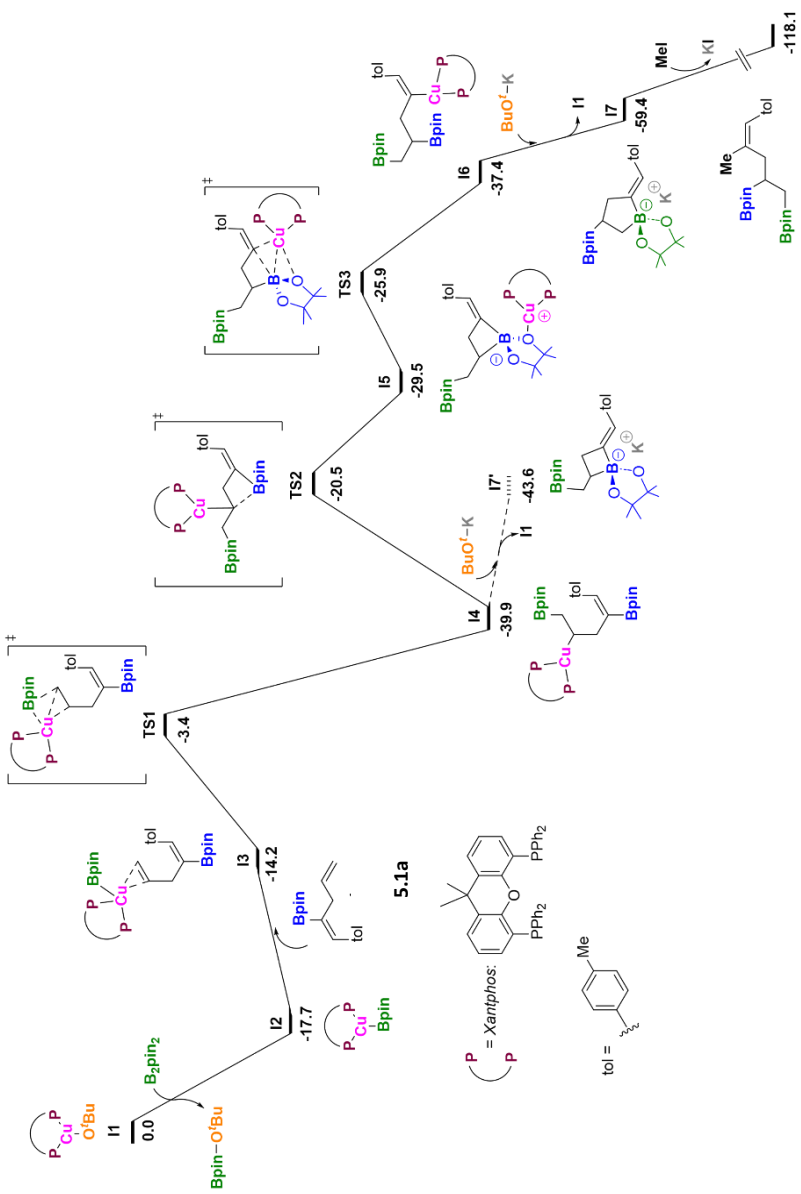
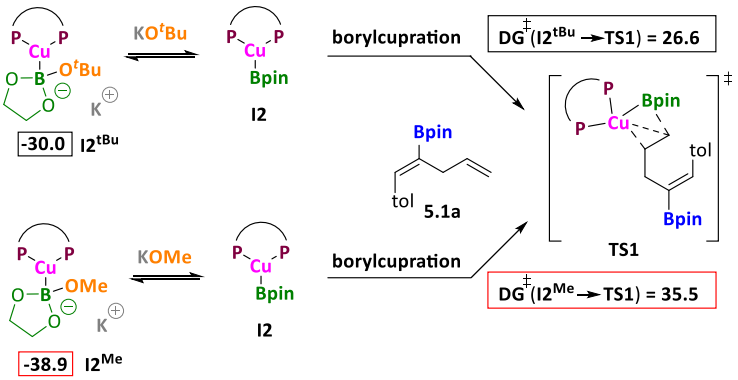


Figure 5.1. Free-energy profile (kcal·mol^{-1}) for the borylcupration of (*Z*)-2-pinacolboryl 1-(*p*-tolyl)penta-1,4-diene (**5.1a**) with B_2pin_2 catalysed by Cu(I)-Xantphos complex in the presence of KO^{t}Bu base. Picture adapted from the DFT calculations performed by R. J. Maza and Prof. J. J. Carbó.

Calculations also reveal that alkoxides from bases (KO^{t}Bu or KOMe) could form Lewis base adducts with the Bpin motifs of the intermediates. Alkoxy coordination on the boryl moiety within intermediate **I2** significantly impacted the reaction outcome by preventing borylcupration at the terminal double bond through transition state **TS1** (Scheme 5.19). Transitioning from KO^{t}Bu to KOMe, the [RO$^-$→**I2**] adduct (**I2**$^{t\text{-Bu}}$ and **I2**^{Me}) became energetically more stable due to reduced steric repulsion between the small Me group and the Cu-Xantphos complex (Scheme 5.19). Consequently, the methoxy adduct **I2**^{Me} formed a deep energy well in the reaction mechanism, resulting in a prohibitive free-energy barrier (**I2**^{Me} → **TS1**) of 35.5 kcal·mol^{-1}.

To sum up, bulky *tert*-butoxide hindered the formation of overly stable adducts due to steric hindrance with the Xantphos ligand, while methoxide strongly interacted and inhibited reaction activity.



Scheme 5.19. DFT calculations were performed by Dr. Ricardo J. Maza and Prof. Jorge J. Carbó. Free-energies (kcal·mol^{-1}) for the coordination of two alkoxides (^{t}BuO$^-$ and MeO$^-$) to the Bpin moiety of intermediate **I2**, and overall free-energy barriers for the borylcupraton in the presence of KO^{t}Bu (**I2**^{tBu} → **TS1**) and KOMe base (**I2**^{Me} → **TS1**).

5.5. Conclusions

We presented a novel 1,3-B/Cu shift mechanism based on a remote rearrangement between C(sp^2)–Bpin and C(sp^3)–Cu fragments, which were generated through the borylcupration of borylated skipped (*Z*)-dienes. This unprecedented carbon-to-carbon boryl migration occurred with stereospecificity around the alkene, facilitating subsequent stereoselective electrophilic trapping by the *in-situ* addition of H^+, alkyl halides, allyl halides, I_2, NBS, or NCS. In addition, mixed diborated products could be synthesised from transborylated skipped (*Z*)-dienes to study the compatibility with different boryl moieties other than pinacolboryl moiety, allowing the synthesis of both regioisomers.

The reaction mechanism has been elucidated through DFT calculations performed by Dr. R. J. Maza and Prof. J. J. Carbó focusing on the sequential borylcupration, 1,3-B/Cu shift, and methylation of borylated skipped (*Z*)-dienes, with particular attention to the role of the base in catalytic activity. Computational studies suggested that the 1,3-B/Cu shift involved a nucleophilic attack of the copper-alkyl moiety on the boron atom bonded to the C(sp^2), forming a 4-membered boracycle structure. Subsequently, copper migrated to the C(sp^2) as the B–C(sp^2) bond opened, producing an alkenyl copper intermediate.

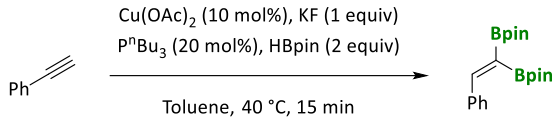
On the other hand, the synthetic application of the novel homoallyl diborated products has been pursued via palladium-catalysed regioselective cross-coupling, producing alkylidenecyclohexanes and alkylidenecyclobutanes. The latter were highly strained, yet stable molecules found in biologically active natural products.

Finally, we attempted to achieve asymmetric induction via 1,3-boryl migration. However, using the (+)-pinanediolboryl moiety as the chiral auxiliary resulted in only a 55:45 enantiomeric ratio.

5.6. Experimental section

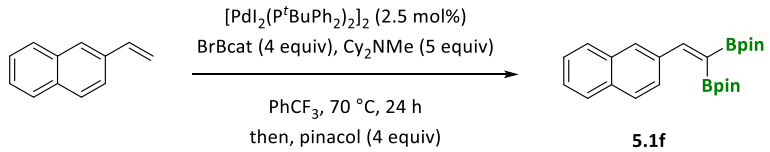
General information. All solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures.[25] Diboron reagents were purchased from Dalian Allychem Co. and were used without further purification. All air-sensitive reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon using Schlenk-type techniques. Flash chromatography purification procedures were performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Analytical Thin Layer Chromatography (TLC) was performed on Merck Kieselgel 60 F254 and was developed using standard visualising agents: UV fluorescence (254 and 366 nm) or potassium permanganate. NMR spectra were recorded at a Varian 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm ^{1}H and 77.16 ppm ^{13}C). ^{11}B NMR chemical shifts (δ) are reported in ppm relative to $BF_3{\cdot}Et_2O$. Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sp = septet, m = multiplet. Melting points were measured using open glass capillaries in a Digital Melting Point IA 9100 apparatus. High-Resolution Mass Spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies with an ESI interface that is located at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona), or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or EI interface that is located at the Unidade de Espectrometría de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela). GC-MS analyses were performed on an 8860 GC System with a 5977B GC/MSD from Agilent Technologies equipped with a capillary column HP-5MS Ultra Inert (30 m, 0.25 mm i.d., 0.25 µm thickness) and using He as the carrier gas.

General procedure for the synthesis of 1,1-diborylalkenes (Method A for 1a, 1b, 1c, 1d, 1e, 1g, 1h) [20]



A Schlenk-tube equipped with a magnetic stir bar was charged with $Cu(OAc)_2$ (10 mol%, 36 mg), KF (116 mg, 2 mmol, 1 equiv) in dry toluene as solvent (2.5 mL). Then, P^nBu_3 (20 mol%, 99 µL), arylacetylene (0.22 mL, 2 mmol), and HBpin (0.58 mL, 4 mmol, 2 equiv) were added in this order. The mixture was stirred for 15 min at 40 °C. The reaction mixture was then diluted with Et_2O and filtered through a plug of celite in the air with copious washing (Et_2O). 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.

General procedure for the synthesis of the 1,1-diborylalkenes (Method B for 1f)[14]

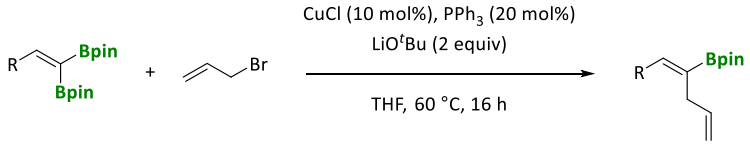


5.1f

A Schlenk tube equipped with a magnetic stir bar was charged with $[PdI_2(P^tBuPh_2)_2]_2$ (41 mg, 2.5 mol%) in dry trifluorotoluene (5 mL) and the solution was stirred at rt for 10 minutes. N,N-dicyclohexylmethylamine (1.1 mL, 5 equiv), a solution of bromocatecholborane in toluene (5 mL, 0.8 M, 4 equiv), and 2-vinyl naphthalene (154 mg, 1 mmol, 1 equiv) were added sequentially. The reaction was stirred in an oil bath at 70 °C for 24 h. At this time, the flask was cooled to rt, opened to air, and charged with pinacol (472 mg, 4 equiv), ammonium pyrrolidine-dithiocarbamate (50 mg, palladium scavenger, 6 equiv to palladium), and diluted with Et_2O (10 mL). The reaction was stirred at rt to 1 h. Then, the reaction was filtered through a pad of celite

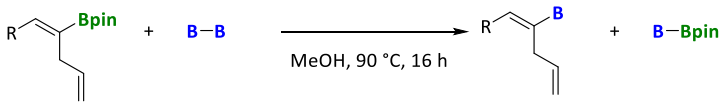
and concentrated in a vacuum at 40 °C to remove all solvents. The resultant crude oil was diluted with Et_2O (20 mL) and washed with 1M aqueous HCl (3 x 20mL) to remove excess amine. The organic layer was dried with $MgSO_4$, filtered through Celite, and concentrated in vacuo. The solvent was gently 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.

General procedure for the synthesis of borylated (*Z*)-skipped dienes[14]



In a flamed Schlenk-tube equipped with a magnetic stir bar, 1,1-diborylalkene (0.2 mmol, 1 equiv), CuCl (2.6 mg, 0.02 mmol, 10 mmol %), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%) and LiO^tBu (32 mg, 0.4 mmol, 2 equiv) were added in THF (4 mL) under argon atmosphere. The reaction mixture was stirred at 60 °C for 10 min and then the allyl bromide (25.9 µL, 0.3 mmol, 1.5 equiv) was introduced into the reaction mixture. After being stirred at 60 °C for 16h, the reaction was concentrated under a vacuum 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.

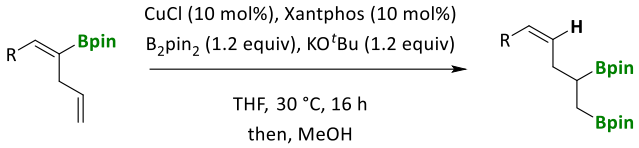
General procedure for the transborylation of 1f to 1f-Bhex[20]



A Schlenk-tube equipped with a magnetic stir bar was charged with the borylated skipped (*Z*)-diene **5.1f** (0.2 mmol, 1 equiv) and the diboron reagent B_2hex_2 or B_2pai_2 (0.4 mmol, 2 equiv) in dry MeOH as solvent (2 mL). The mixture was stirred for 16 h at 90 °C. The solvent was gently concentrated at the rotary evaporator and the NMR

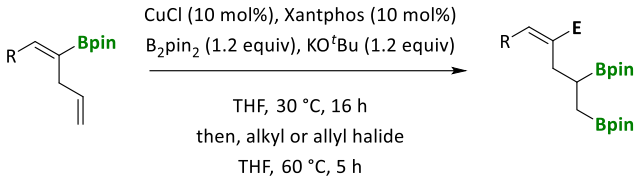
yield was calculated by comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product **5.1f-Bhex** and **5.45**.

General procedure for Cu-catalysed borylcupration – 1,3-B/Cu shift – protonation



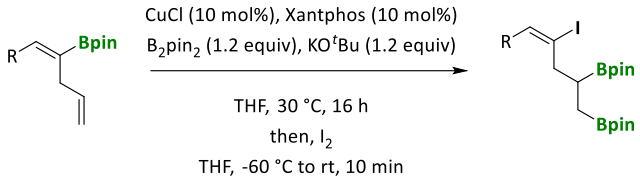
CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added in the vial through the rubber septum. Then, the borylated (*Z*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C. After the reaction was complete, the reaction mixture was filtered over Celite. The organic extracts were 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.

General procedure for Cu-catalysed borylcupration – 1,3-B/Cu shift – electrophilic trapping with alkyl or allyl halides



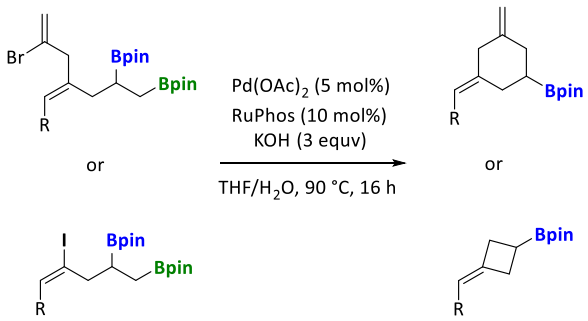
CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1 M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added in the vial through the rubber septum. Then, the borylated (*Z*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C and stirred for 16 hours. Subsequently, the corresponding electrophile (4 equiv, 0.8 mmol) was added, and the temperature was raised to 60 °C. The mixture was allowed to react for 5 hours at 60 °C until the reaction was completed and then filtered over Celite. The organic extracts were then concentrated under vacuum and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

General procedure for Cu-catalysed borylcupration – 1,3-B/Cu shift – electrophilic trapping with I_2



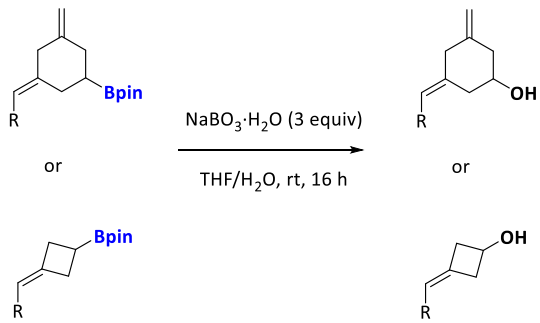
CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added to the vial through the rubber septum. Then, the borylated (*Z*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C and stirred for 16 hours. Subsequently, iodine (101.5 mg, 2 equiv, 0.4 mmol) was dissolved in 2 mL of THF in a second oven-dried flask. The reaction mixture was then kept at -60 °C while the iodine solution was passed through a Teflon tubing. The cooling bath was removed, and the temperature was allowed to rise to room temperature. After 10 minutes at room temperature, a mixture of 10 mL of saturated aqueous ammonium chloride and 1 mL of saturated sodium bisulfite is added with vigorous stirring. The mixture is filtered through Celite by suction and the contents of the funnel were washed with Et_2O (3 x 15 mL). The inorganic layer is washed twice with pentane. The organic extracts were dried over anhydrous magnesium sulphate and then concentrated under vacuum. The NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

General procedure for intramolecular Suzuki-Miyaura cross-coupling[21]



In a flamed Schlenk-tube equipped with a magnetic stir bar, $Pd(OAc)_2$ (2.25 mg, 5 mol%), RuPhos (9.33, 10 mol%), and the substrate (0.2 mmol) were added in THF (2 mL). Under an argon atmosphere, KOH (33.6 mg, 0.6 mmol, 3 equiv) and deoxygenated water (0.2 mL) were added. The reaction mixture was stirred at 90°C for 16 h. After that, the mixture was concentrated under vacuum and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

General procedure for the oxidation reaction

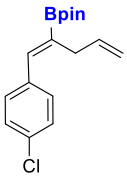


In an opened-air flask, charged with a magnetic stir bar, were added the corresponding alkylidenecyclobutanes (0.1 mmol, 1 equiv), $NaBO_3{\cdot}H_2O$ (0.3 mmol, 3 equiv), THF (2 mL) and distilled water (1 mL). The reaction was closed with a septum with a needle to avoid over pressures and was stirred for 16 h at room temperature. After this time, the mixture was extracted with Et_2O (3 x 15 mL), the organic layer was dried with anhydrous magnesium sulphate, filtered and the solvents were evaporated.

The crude residue was purified by silica gel chromatography to obtain the corresponding product.

- Characterisation of borylated (*Z*)-skipped dienes[14]

(*Z*)-2-(1-(4-Chlorophenyl)penta-1,4-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.1d)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (29 mg, 47%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (m, 4H), 6.07 – 5.89 (m, 1H), 5.09 – 4.98 (m, 2H), 3.11 – 3.06 (m, 2H), 1.29 (s, 12H).

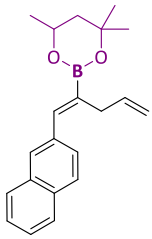
^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.8, 137.0, 130.2, 128.3, 114.8, 83.6, 33.5, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.62.

HRMS-(ESI+) for **$C_{17}H_{23}BClO_2$ $[M+H]^+$:** calculated: 305.1479; found: 305.1484.

- Characterisation of transborylated products

(*Z*)-4,4,6-trimethyl-2-(1-(naphthalen-2-yl)penta-1,4-dien-2-yl)-1,3,2-dioxaborinane (5.1f-Bhex)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (31 mg, 48%).

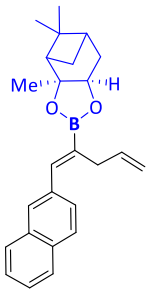
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 – 7.75 (m, 4H), 7.58 – 7.37 (m, 4H), 6.06 (ddt, J = 17.3, 10.1, 6.0 Hz, 1H), 5.17 – 5.00 (m, 2H), 4.29 (m, 1H), 3.16 (d, J = 4.4 Hz, 2H), 1.83 (dd, J = 13.9, 3.0 Hz, 1H), 1.59 (dd, J = 13.9, 13.8 Hz, 1H), 1.34 (s, 3H), 1.34 (s, 3H), 1.32 (d, J = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.2, 138.3, 135.8, 133.2, 132.3, 128.1, 127.7, 127.5, 127.3, 127.3, 125.8, 125.7, 114.3, 70.8, 64.9, 45.9, 33.6, 31.2, 28.1, 23.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 26.1.

HRMS-(ESI+) for **$C_{21}H_{26}BO_2$ $[M+H]^+$:** calculated: 321.2025; found: 321.2028.

(3aS,7aR)-3a,5,5-Trimethyl-2-((*Z*)-1-(naphthalen-2-yl)penta-1,4-dien-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (5.45)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (45 mg, 60%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 – 7.78 (m, 4H), 7.56 (s, 1H), 7.58 – 7.43 (m, 3H), 6.14 (dddd, J = 17.5, 7.2, 5.6, 2.8 Hz, 1H), 5.26 – 5.07 (m, 2H), 4.42 (dd, J = 8.8, 1.9 Hz, 1H), 3.28 – 3.24 (m, 2H), 2.47 – 2.37 (m, 1H), 2.34 – 2.23 (m, 1H), 2.20 – 2.12 (m, 1H), 2.00 – 1.93 (m, 2H), 1.49 (s, 3H), 1.34 (s, 3H), 1.31 – 1.22 (m, 1H), 0.90 (s, 3H).

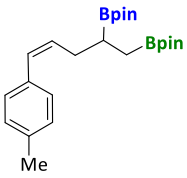
^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.38, 137.44, 135.06, 133.25, 132.61, 128.26, 128.03, 127.61, 127.59, 127.11, 126.04, 115.00, 86.03, 78.14, 51.42, 39.57, 38.20, 35.70, 33.89, 28.76, 27.14, 26.58, 24.09.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.92.

HRMS-(ESI+) for **$C_{25}H_{30}BO_2$ [M+H]$^+$:** calculated: 373.2333; found: 373.2325.

- Characterisation data for products of Cu-catalysed borylcupration - 1,3-B/Cu shift – protonation or electrophilic trapping

(*Z*)-2,2'-(5-(p-Tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.2)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (71 mg, 87%).

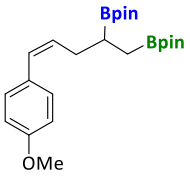
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.36 (dd, J = 11.7, 2.0 Hz, 1H), 5.62 (dt, J = 11.7, 7.3 Hz, 7.3 Hz, 1H), 2.44 (m, 2H), 2.32 (s, 3H), 1.23 (s, 6H) 1.22 (s, 6H), 1.21 (m, 1H), 1.19 (s, 12H), 0.95 – 0.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8, 135.0, 132.4, 128.8, 128.8, 128.7, 82.9, 82.8, 32.3, 24.8, 24.8, 24.7, 24.7, 21.1, 19.3 (C-B), 12.5 (C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 413.3029; found: 413.3050.

(*Z*)-2,2'-(5-(4-Methoxyphenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.3)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (83 mg, 97%).

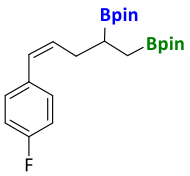
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.20 (m, 2H), 6.88 – 6.80 (m, 2H), 6.32 (dt, J = 11.7, 1.9 Hz, 1H), 5.57 (dt, J = 11.7, 7.3 Hz, 7.3 Hz, 1H), 3.79 (s, 3H), 2.42 (m, 2H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (m, 1H), 1.18 (s, 12H), 1.01 – 0.78 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 131.5, 130.6, 130.0, 128.4, 113.4, 82.9, 82.8, 55.2, 32.3, 24.8, 24.8, 24.7, 24.7, 19.1 (C-B), 12.5 (C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_5$ [M+H]$^+$:** calculated: 429.2978; found: 429.2990.

(*Z*)-2,2'-(5-(4-Fluorophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.4)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (75 mg, 90%).

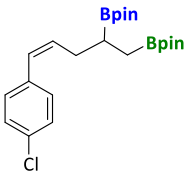
^{1}H NMR ($CDCl_3$, 400 MHz) δ7.57 – 7.51 (m, 2H), 7.26 (m, 2H), 6.63 (dd, J = 11.7, 2.0 Hz, 1H), 5.94 (dt, J = 11.7, 7.3, 7.3 Hz, 1H), 2.68 (m, 2H), 1.50 (s, 6H), 1.50 (s, 6H), 1.50 (m, 1H) 1.47 (s, 12H), 1.20 – 1.11 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3 (d, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 133.9, 133.9, 133.0, 130.4 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 127.9, 114.7 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 83.0, 82.8, 32.1, 24.8, 24.8, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5.

HRMS-(ESI+) for **$C_{23}H_{36}B_2O_4$ [M+H]$^+$**: calculated: 417.2778; found: 417.2777.

(*Z*)-2,2'-(5-(4-Chlorophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.5)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (75 mg, 87%).

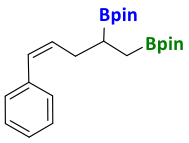
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 4H), 6.35 (dt, J = 11.4, 1.9 Hz, 1H), 5.70 (dt, J = 11.7, 7.3, 7.3 Hz, 1H), 2.41 (m, 2H), 1.23 (s, 6H), 1.23 (s, 6H), 1.23 (m, 1H), 1.19 (s, 12H), 0.92 – 0.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 133.8, 131.9, 130.1, 128.1, 127.8, 83.0, 82.9, 32.1, 24.8, 24.8, 24.7, 24.7, 24.7.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.5.

HRMS-(ESI+) for **$C_{23}H_{36}B_2ClO_4$ [M+H]$^+$:** calculated: 433.2483; found: 433.2501.

(*Z*)-2,2'-(5-Phenylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.6)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (69 mg, 87%).

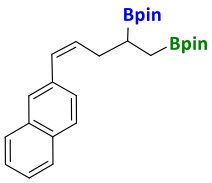
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 4.4 Hz, 4H), 7.21 – 7.15 (m, 1H), 6.39 (dt, J = 11.7, 1.9 Hz, 1H), 5.67 (dt, J = 11.7, 7.3, 7.3 Hz, 1H), 2.44 (dddd, J = 17.2, 15.1, 7.5, 1.9 Hz, 2H), 1.22 (s, 6H), 1.22 (s, 6H), 1.22 (m, 1H), 1.18 (s, 12H), 0.97 – 0.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 133.1, 129.0, 128.8, 127.9, 126.1, 82.9, 82.8, 32.2, 24.8, 24.8, 24.7, 24.7.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.8.

HRMS-(ESI+) for **$C_{23}H_{37}B_2O_4$ [M+H]$^+$**: calculated: 399.2872; found: 399.2883.

(Z)-2,2'-(5-(Naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.7)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (67 mg, 75%).

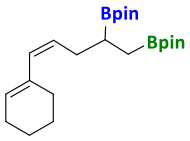
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 – 7.71 (m, 4H), 7.49 – 7.39 (m, 3H), 6.58 – 6.52 (m, 1H), 5.76 (dt, J = 11.7, 7.3 Hz, 7.3 Hz, 1H), 2.63 – 2.37 (m, 2H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (m, 1H), 1.16 (s, 12H), 0.99 – 0.81 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.4, 133.6, 133.3, 132.0, 129.0, 127.9, 127.5, 127.4, 127.3, 125.8, 125.4, 83.0, 82.8, 32.4, 24.8, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.3.

HRMS-(ESI+) for **$C_{27}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 449.3034; found: 449.3041.

(*Z*)-2,2'-(5-(Cyclohex-1-en-1-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.8)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (92 mg, 87%).

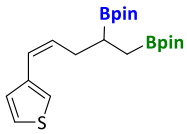
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (d, , J = 11.8, Hz, 1H), 5.59 (m, 1H), 5.24 (dt, J = 11.8, 7.4, 7.4 Hz, 1H), 2.33 (m, 2H), 2.19 – 2.04 (m, 4H), 1.64 – 1.49 (m, 4H), 1.22 (s, 24H), 1.21 (m, 1H), 0.91 – 0.80 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.6, 131.9, 129.4, 127.0, 82.9, 82.8, 32.8, 28.9, 25.6, 24.9, 24.8, 24.8, 24.7, 22.9, 22.1, 19.1, 12.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{23}H_{41}B_2O_4$ [M+H]$^+$:** calculated: 403.3185; found: 403.3208.

(*Z*)-2,2'-(5-(Thiophen-3-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.9)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (56 mg, 68%).

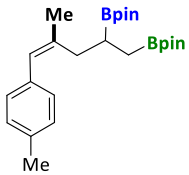
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.14 – 7.10 (m, 1H), 6.33 (dd, J = 11.7, 1.9 Hz, 1H), 5.62 (dt, J = 11.6, 7.3, 7.3 Hz, 1H), 2.45 (m, 2H), 1.22 (s, 6H), 1.22 (s, 6H), 1.22 (m, 1H), 1.21 (s, 12H), 0.96 – 0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 132.1, 128.9, 124.4, 123.0, 122.5, 83.0, 82.9, 32.7, 24.8, 24.7, 24.7, 24.7.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.8.

HRMS-(ESI+) for **$C_{21}H_{35}B_2O_4S$ [M+H]$^+$:** calculated: 405.2437; found: 405.2442.

(*Z*)-2,2'-(4-Methyl-5-(p-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.10)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (78 mg, 92%).

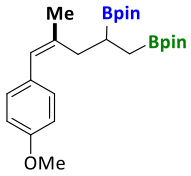
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 2.44 – 2.35 (m, 2H), 2.31 (s, 3H), 1.85 (s, 3H), 1.26 – 1.23 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.18 (s, 12H), 0.80 – 0.75 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3, 135.7, 135.0, 128.8, 128.6, 126.3, 82.9, 82.8, 35.4, 24.9, 24.7, 24.7, 23.7, 21.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.7.

HRMS-(ESI+) for **$C_{25}H_{42}B_2O_4$ [M+H]$^+$:** calculated: 427.3185; found: 427.3209.

(*Z*)-2,2'-(5-(4-Methoxyphenyl)-4-methylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.11)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (85 mg, 96%).

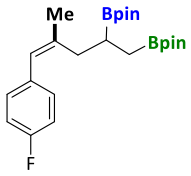
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.23 (s, 1H), 3.78 (s, 3H), 2.45 – 2.37 (m, 1H), 2.31 (m, 1H), 1.84 (s, 3H), 1.20 (s, 6H), 1.20 (s, 6H), 1.20 (m, 1H), 1.18 (s, 12H), 0.81 – 0.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 137.6, 131.2, 130.0, 125.8, 113.3, 82.9, 82.8, 55.1, 35.3, 24.8, 24.7, 24.7, 24.6, 23.7.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.2.

HRMS-(ESI+) for **$C_{25}H_{41}B_2O_5$ [M+H]$^+$:** calculated 443.3135; found: 443.3153.

(*Z*)-2,2'-(4-Methyl-5-(p-fluoro)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.12)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (69 mg, 80%).

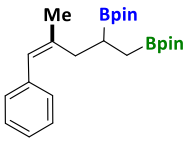
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 6.99 – 6.90 (m, 2H), 6.23 (s, 1H), 2.38 (dd, J = 13.7, 7.2 Hz, 1H), 2.27 (dd, J = 13.7, 8.9 Hz, 1H), 1.84 (s, 3H), 1.42 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 0.79 – 0.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 139.0, 134.5, 134.5, 130.4 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 125.3, 114.6 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 82.9, 82.8, 35.2, 24.8, 24.8, 24.7, 24.7, 24.7, 24.6, 24.6, 23.6, 16.2 (C-B), 12.2 (C-B).

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.7.

HRMS-(ESI+) for **$C_{24}H_{38}B_2FO_4$ [M+H]$^+$:** calculated: 431.2935; found: 431.2940.

(*Z*)-2,2'-(4-Methyl-5-phenylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.13)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (73 mg, 91%).

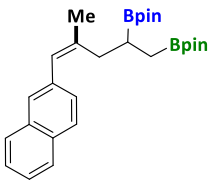
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 4H), 7.14 (m, 1H), 6.30 (s, 1H), 2.43 (dd, J = 13.6, 7.2, Hz, 1H), 2.38 – 2.30 (m, 1H), 1.87 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H), 1.20 (m, 1H), 1.19 (s, 12H), 0.84 – 0.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.6, 128.9, 128.8, 127.8, 126.5, 125.5, 82.9, 82.8, 35.3, 24.8, 24.7, 24.7, 24.6, 23.7.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.2.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 413.3029; found: 413.3036.

(*Z*)-2,2'-(4-Methyl-5-(naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.14)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (85 mg, 92%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 – 7.72 (m, 4H), 7.45 – 7.37 (m, 3H), 6.45 (s, 1H), 2.53 (dd, J = 13.8, 7.3 Hz, 1H), 2.41 (dd, J = 13.7, 8.9 Hz, 1H), 1.93 (s, 3H), 1.25 (m, 1H), 1.20 (s, 6H), 1.15 (s, 6H), 1.15 (s, 12H), 0.87 – 0.79 (m, 2H).

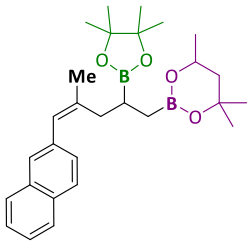
^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.6, 136.2, 133.5, 131.8, 127.9, 127.8, 127.4, 127.2, 126.5, 125.6, 125.1, 83.0, 82.8, 35.5, 24.9, 24.8, 24.7, 23.9.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.4.

HRMS-(ESI+) for **$C_{28}H_{42}B_2O_4$ [M+H]$^+$:** calculated: 463.3185; found: 463.3197.

(*Z*)-4,4,6-Trimethyl-2-(4-methyl-5-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)-1,3,2-dioxaborinane

(5.14-BpinBhex)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (47 mg, 51%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 – 7.71 (m, 4H), 7.49 – 7.33 (m, 3H), 6.43 (m, 1H), 3.98 (m, 1H), 2.54 – 2.42 (m, 2H), 1.93 (s, 3H), 1.68 (m, 1H), 1.64 – 1.50 (m, 2H), 1.33 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H), 1.16 (d, J = 1.6 Hz, 6H), 0.76 – 0.71 (m, 2H).

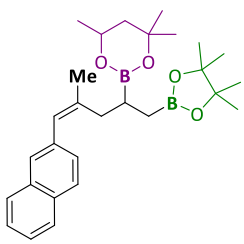
^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.2, 136.3, 133.5, 131.7, 127.9, 127.4, 127.2, 127.2, 126.2, 126.1, 125.6, 125.0, 82.7, 70.2, 64.2, 45.7, 38.8, 35.2, 31.1, 28.0, 28.0, 25.1, 25.0, 24.7, 24.6, 23.9, 23.2, 23.1, 16.4 (C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.1.

HRMS-(ESI+) for **$C_{28}H_{41}B_2O_4$ [M+H]$^+$:** calculated: 463.3185; found: 463.3149.

(*Z*)-4,4,6-Trimethyl-2-(4-methyl-5-(naphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-1,3,2-dioxaborinane

(5.14-BhexBpin)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (87 mg, 95%).

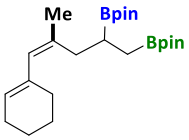
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 – 7.70 (m, 5H), 7.52 – 7.34 (m, 3H), 6.39 (s, 1H), 4.07 (m, 1H), 2.61 – 2.40 (m, 1H), 2.40 – 2.23 (m, 1H), 1.92 (d, J = 1.5 Hz, 3H), 1.70 – 1.59 (m, 1H), 1.33 – 1.30 (m, 1H), 1.21 (s, 3H), 1.21 (s, 3H), 1.18 (s, 3H), 1.16 (s, 3H), 1.16 (s, 3H), 1.16 (m, 1H), 1.15 (s, 6H), 0.85 – 0.70 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 136.9, 133.5, 131.9, 128.0, 127.8, 127.4, 127.1, 127.0, 125.6, 125.5, 125.0, 82.6, 70.2, 65.3, 45.7, 39.7, 36.5, 31.2, 27.9, 24.9, 24.8, 24.8, 24.7, 24.7, 24.3, 23.3, 22.9, 22.3.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5, 30.4.

HRMS-(ESI+) for **$C_{28}H_{41}B_2O_4$ [M+H]$^+$:** calculated: 463.3185; found: 463.3190.

(*Z*)-2,2'-(5-(Cyclohex-1-en-1-yl)-4-methylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.15)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (74 mg, 89%).

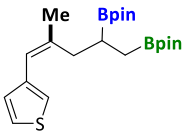
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 5.51 (m, 1H), 2.30 (dd, J = 8.1, 4.0 Hz, 2H), 2.10 – 2.01 (m, 3H), 1.71 (s, 3H), 1.62 – 1.50 (m, 5H), 1.22 (s, 24H), 1.22 (m, 1H), 0.81 – 0.71 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 135.2, 129.5, 125.2, 82.8, 82.7, 35.7, 29.3, 25.5, 24.9, 24.8, 24.7, 24.7, 23.8, 23.0, 22.2.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 35.0.

HRMS-(ESI+) for **$C_{24}H_{43}B_2O_4$ [M+H]$^+$:** calculated: 417.3342; found: 417.3358.

(*Z*)-2,2'-(4-Methyl-5-(thiophen-3-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.16)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (58 mg, 70%).

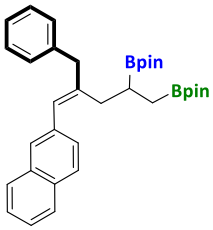
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.07 (dd, J = 4.7, 1.6 Hz, 1H), 6.20 (s, 1H), 2.50 (dd, J = 13.6, 7.7 Hz, 1H), 2.34 (dd, J = 13.6, 8.7 Hz, 1H), 1.85 (s, 3H), 1.21 (m, 1H), 1.20 (s, 24H), 0.86 – 0.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.9, 129.1, 124.1, 121.5, 120.6, 83.0, 82.8, 36.1, 24.9, 24.9, 24.7, 24.6, 24.1.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.1.

HRMS-(ESI+) for **$C_{22}H_{37}B_2O_4S$ [M+H]$^+$:** calculated: 419.2593; found: 419.2602.

(*E*)-2,2'-(4-Benzyl-5-(naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.17)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil from benzyl bromide (47 mg, 44%) and benzyl iodide (97 mg, 90%).

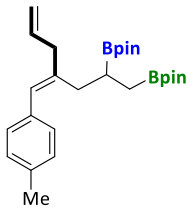
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 – 7.70 (m, 4H), 7.49 – 7.36 (m, 3H), 7.32 (m, 5H), 6.42 (s, 1H), 3.58 (d, J = 1.3 Hz, 2H), 2.62 – 2.49 (m, 1H), 2.39 – 2.28 (m, 1H), 1.36 – 1.29 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H), 1.15 (s, 6H), 1.14 (s, 6H), 0.85 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 140.2, 135.8, 133.4, 131.8, 129.3, 128.2, 127.9, 127.9, 127.4, 127.2, 125.9, 125.6, 125.2, 83.0, 82.8, 43.1, 33.7, 24.9, 24.8, 24.7, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.0.

HRMS-(ESI+) for **$C_{34}H_{46}B_2O_4$ [M+H]$^+$:** calculated: 539.3498; found: 539.3508.

(*E*)-2,2'-(4-(4-Methylbenzylidene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.18)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil. Using allyl bromide as the electrophile (71 mg, 78%).

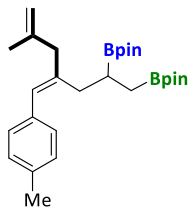
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 6.26 (s, 1H), 5.90 (ddt, J = 16.9, 10.1, 6.9 Hz, 1H), 5.16 – 5.01 (m, 2H), 2.92 (d, J = 6.9 Hz, 2H), 2.46 (dd, J = 13.7, 7.6 Hz, 1H), 2.32 (d, J = 2.1 Hz, 1H), 2.31 (s, 3H), 1.19 (s, 24H), 1.19 (m, 1H), 0.85 – 0.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.9, 135.5, 135.2, 128.9, 128.6, 126.5, 115.9, 82.9, 82.8, 40.9, 33.9, 24.9, 24.8, 24.7, 24.6, 21.0.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.8.

HRMS-(ESI+) for **$C_{27}H_{43}B_2O_4$ [M+H]$^+$:** calculated: 453.3342; found: 453.3358.

(*E*)-2,2'-(6-Methyl-4-(4-methylbenzylidene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.19)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (88 mg, 94%).

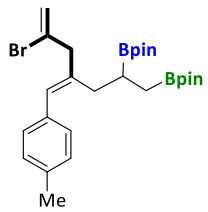
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.28 (s, 1H), 4.83 (d, J = 1.4 Hz, 2H), 2.88 (s, 2H), 2.44 (dd, J = 13.7, 7.6 Hz, 1H), 2.31 (s, 3H), 2.30 – 2.24 (m, 1H), 1.72 (s, 3H), 1.19 (s, 24H), 1.19 (m, 1H), 0.83 – 0.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.6, 135.5, 135.2, 128.9, 128.6, 127.5, 112.3, 82.8, 82.8, 45.5, 33.3, 24.9, 24.8, 24.7, 24.6, 22.0, 21.0.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.2.

HRMS-(ESI+) for **$C_{28}H_{45}B_2O_4$ [M+H]$^+$:** calculated: 467.3498; found: 467.3500.

(*E*)-2,2'-(6-Bromo-4-(4-methylbenzylidene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.20a)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (63 mg, 61%).

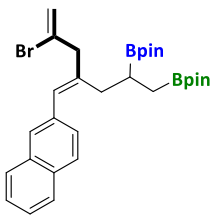
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.37 (s, 1H), 5.73 (d, J = 1.5 Hz, 1H), 5.52 (d, J = 1.5 Hz, 1H), 3.31 (s, 2H), 2.49 (dd, J = 13.9, 7.7 Hz, 1H), 2.32 (s, 3H), 2.31 – 2.22 (m, 1H), 1.46 – 1.35 (m, 1H), 1.19 (s, 24H), 0.81 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.7, 134.9, 132.7, 129.7, 128.9, 128.7, 118.3, 82.9, 82.8, 48.6, 32.9, 24.9, 24.9, 24.7, 24.6, 21.1.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.2.

HRMS-(ESI+) for **$C_{27}H_{42}B_2BrO_4$ [M+H]$^+$:** calculated: 531.2447; found: 531.2447.

(*E*)-2,2'-(6-Bromo-4-(naphthalen-2-ylmethylene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.20f)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (107 mg, 95%).

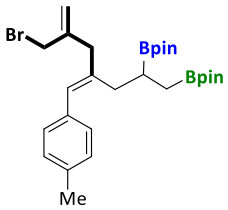
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.72 (m, 4H), 7.44 (m, 3H), 6.57 (s, 1H), 5.78 (s, 1H), 5.57 (s, 1H), 3.38 (s, 2H), 2.59 (dd, J = 13.9, 7.7 Hz, 1H), 2.40 (dd, J = 13.8, 8.7 Hz, 1H), 1.19 (s, 6H), 1.19 (s, 6H), 1.19 (m, 1H), 1.16 (s, 6H), 1.15 (s, 6H), 0.90 – 0.81 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.4, 135.4, 133.4, 132.5, 132.0, 129.7, 127.9, 127.6, 127.5, 127.4, 127.4, 125.7, 125.4, 118.6, 83.0, 82.9, 48.7, 33.1, 24.9, 24.8, 24.7, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{30}H_{42}B_2BrO_4$ [M+H]$^+$:** calculated: 568.1781; found: 568.1790.

(*E*)-2,2'-(6-(Bromomethyl)-4-(4-methylbenzylidene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.21)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (100 mg, 97%).

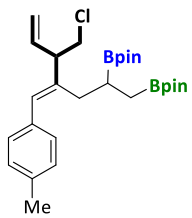
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.36 (s, 1H), 5.28 (d, J = 1.4 Hz, 1H), 5.12 (d, J = 1.5 Hz, 1H), 4.00 (s, 2H), 3.11 (m, 2H), 2.43 (dd, J = 13.7, 7.6 Hz, 1H), 2.32 (s, 3H), 2.30 – 2.23 (m, 1H), 1.19 (s, 24H), 1.19 (m, 1H), 0.80 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.4, 135.5, 135.0, 128.9, 128.6, 117.5, 82.9, 82.8, 41.0, 36.1, 33.0, 24.9, 24.8, 24.7, 24.6, 21.1, 18.5, 11.1.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.6.

HRMS-(ESI+) for **$C_{28}H_{43}B_2BrO_4$ [M+H]$^+$:** calculated: 545.2604; found: 545.2596.

(*E*)-2,2'-(5-(Chloromethyl)-4-(4-methylbenzylidene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.22)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (59 mg, 59%) as a mixture of diastereosiomers.

Major product: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (m, 2H), 7.08 (m, 2H), 6.27 (s, 1H), 5.96 – 5.79 (m, 1H), 5.28 – 5.14 (m, 2H), 3.77 (m, 1H), 3.61 (m, 1H), 3.31 (m, 1H), 2.53 (dd, J = 13.9, 8.2 Hz, 1H), 2.44 – 2.36 (m, 1H), 2.31 (s, 3H), 1.19 (s, 12H), 1.18 (s, 12H), 1.18 (m, 1H), 0.85 – 0.77 (m, 2H). Minor product: **^{1}H NMR** (400

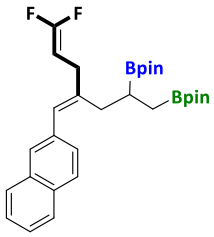
MHz, $CDCl_3$) δ 7.16 (m, 2H), 7.08 (m, 2H), 6.30 (s, 1H), 5.96 – 5.79 (m, 1H), 5.28 – 5.14 (m, 2H), 3.77 (m, 1H), 3.71 – 3.57 (m, 1H), 3.23 (m, 1H), 2.44 – 2.36 (m, 1H), 2.31 (s, 3H), 2.31 – 2.29 (m, 1H), 1.20 (s, 12H), 1.20 (s, 12H), 1.19 (m, 1H), 0.85 – 0.77 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.1, 134.8, 128.9, 128.9, 128.7, 127.5, 116.6, 116.5, 83.0, 82.9, 50.1, 49.8, 46.8, 34.0, 24.9, 24.8, 24.7, 24.7, 24.7, 24.6, 21.1.

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.9.

HRMS-(ESI+) for **$C_{28}H_{44}B_2ClO_4$ [M+H]$^+$:** calculated: 501.3109; found: 501.3110.

(*E*)-2,2'-(7,7-Difluoro-4-(naphthalen-2-ylmethylene)hept-6-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.23)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (59 mg, 56%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (m, 4H), 7.50 – 7.37 (m, 3H), 6.46 (s, 1H), 4.38 (dt, J = 25.2, 7.9, 7.9 Hz, 1H), 2.92 (d, J = 7.9 Hz, 2H), 2.57 (dd, J = 13.9, 8.0 Hz, 1H), 2.38 (dd, J = 13.9, 8.5 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 1.15 (s, 6H), 1.15 (s, 6H), 1.14 (m, 1H), 0.87 – 0.78 (m, 2H).

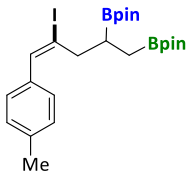
^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.6 (dd, $^1J_{C-F}$ = 286.3, 286.7 Hz), 146.5, 140.7, 135.6, 133.4, 131.9, 127.9, 127.7, 127.4, 127.3, 126.4, 125.7, 125.3, 83.0, 82.8, 76.41 (dd, $^2J_{C-F}$ = 22.0, 19.0 Hz), 34.1, 29.7, 29.4, 29.3, 24.9, 24.8, 24.6, 24.6 24.5 (d, $^3J_{C-F}$ = 6.4 Hz), 16.6 (C-B), 12.6 (C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.3.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -88.16 (d, *J* = 45.2 Hz), -91.46 (dd, *J* = 45.2, 26.3 Hz).

HRMS-(ESI+) for **$C_{30}H_{41}B_2F_2O_4$ [M+H]$^+$:** calculated: 525.3154; found: 525.3148.

(*E*)-2,2'-(4-Iodo-5-(p-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.24)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (95 mg, 89%).

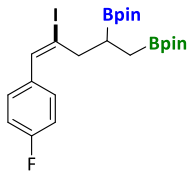
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (s, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.67 (ddd, J = 14.4, 5.9, 1.5 Hz, 1H), 2.56 (ddd, J = 14.5, 9.2, 1.0 Hz, 1H), 2.30 (s, 3H), 1.65 – 1.53 (m, 1H), 1.20 (s, 6H), 1.20 (s, 6H), 1.16 (s, 6H), 1.13 (s, 6H), 0.93 – 0.83 (m, 1H), 0.73 (dd, J = 16.1, 9.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.5, 136.6, 135.1, 128.9, 128.3, 111.3, 83.1, 82.9, 41.0, 24.9, 24.8, 24.7, 21.2, 19.9, 10.9.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.3.

HRMS-(ESI+) for **$C_{24}H_{38}B_2IO_4$ $[M+H]^+$:** calculated: 539.1995; found: 539.2012.

(*E*)-2,2'-(4-Iodo-5-(p-fluoro)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.25)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (100 mg, 92%).

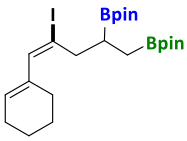
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24 – 7.18 (m, 2H), 6.99 – 6.92 (m, 2H), 2.62 (ddd, J = 14.5, 6.0, 1.5 Hz, 1H), 2.46 (ddd, J = 14.5, 9.2, 1.0 Hz, 1H), 1.62 – 1.50 (m, 1H), 1.17 (s, 6H), 1.17 (s, 6H), 1.13 (s, 6H), 1.11 (s, 6H), 0.85 (dd, J = 16.0, 4.9 Hz, 1H), 0.69 (dd, J = 16.0, 9.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, $^{1}J_{C\text{-}F}$ = 246.7 Hz), 140.3, 133.9, 133.9, 130.1 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 111.9, 111.9, 83.1, 82.9, 40.8, 24.8, 24.7, 24.7, 24.7

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.4.

HRMS-(ESI+) for **$C_{23}H_{35}B_2FIO_4$ [M+H]$^+$:** calculated: 543.1745; found: 543.1746.

(*E*)-2,2'-(5-(Cyclohex-1-en-1-yl)-4-iodopent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.26)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (102 mg, 97%).

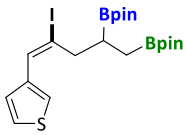
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.62 (m, 1H), 2.61 (ddd, J = 14.4, 6.1, 1.3 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.12 – 1.98 (m, 3H), 1.64 – 1.49 (m, 5H), 1.22 (s, 12H), 1.21 (s, 12H), 1.21 (m, 1H), 0.92 – 0.81 (m, 1H), 0.76 – 0.66 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 137.1, 136.1, 136.1, 128.6, 128.6, 108.4, 105.0, 83.0, 83.0, 82.8, 49.4, 42.0, 28.5, 25.5, 24.9, 24.8, 24.8, 24.7, 22.6, 21.8.

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.4.

HRMS-(ESI+) for **$C_{23}H_{40}B_2IO_4$ [M+H]$^+$:** calculated: 529.2152; found: 529.2165.

(*E*)-2,2'-(4-Iodo-5-(thiophen-3-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.27)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (102 mg, 96%).

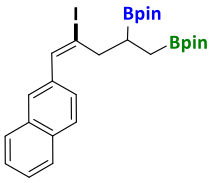
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.24 – 7.19 (m, 2H), 7.09 (dd, J = 5.0, 1.3 Hz, 1H), 2.79 (ddd, J = 14.4, 6.5, 1.2 Hz, 1H), 2.60 (ddd, J = 14.5, 8.9, 0.9 Hz, 1H), 1.62 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.20 (m, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.93 (dd, J = 16.0, 5.1 Hz, 1H), 0.81 (dd, J = 16.0, 9.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 135.5, 128.2, 124.8, 123.4, 110.4, 83.1, 82.9, 42.0, 24.9, 24.8, 24.7, 24.6.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.9.

HRMS-(ESI+) for **$C_{21}H_{34}B_2IO_4S$ [M+H]$^+$:** calculated: 531.1403; found: 531.1393.

(*E*)-2,2'-(4-Iodo-5-(naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.28)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (111 mg, 97%).

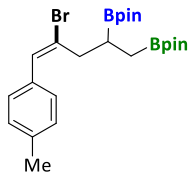
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.73 (m, 4H), 7.51 (s, 1H), 7.48 – 7.37 (m, 3H), 2.78 (ddd, J = 14.5, 6.0, 1.4 Hz, 1H), 2.65 (ddd, J = 14.4, 9.1, 1.0 Hz, 1H), 1.69 – 1.59 (m, 1H), 1.21 (s, 6H), 1.21 (m, 1H), 1.20 (s, 6H), 1.09 (s, 6H), 1.05 (s, 6H), 0.95 – 0.89 (m, 1H), 0.77 (dd, J = 16.0, 9.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.5, 135.3, 133.2, 132.2, 127.7, 127.5, 127.3, 126.6, 126.1, 125.9, 112.4, 83.1, 82.8, 41.1, 24.8, 24.7, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{27}H_{38}B_2IO_4$ [M+H]$^+$:** calculated: 575.1995; found: 575.2000.

(*E*)-2,2'-(4-Bromo-5-(p-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.29)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (80 mg, 81%).

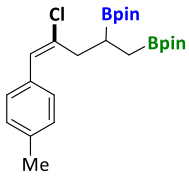
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.97 (s, 1H), 2.82 – 2.66 (m, 2H), 2.31 (s, 3H), 1.67 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.16 (s, 6H), 1.15 (s, 6H), 0.95 – 0.87 (m, 1H), 0.78 (dd, J = 16.0, 9.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 133.7, 133.0, 131.1, 128.9, 128.4, 83.1, 82.8, 38.5, 24.8, 24.8, 24.7, 21.1.

^{11}B NMR (129 MHz, $CDCl_3$) δ 33.8.

HRMS-(ESI+) for **$C_{24}H_{38}B_2BrO_4$ $[M+H]^+$:** calculated: 491.2134; found: 491.2128.

(*E*)-2,2'-(4-Chloro-5-(p-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.30)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (69 mg, 77%).

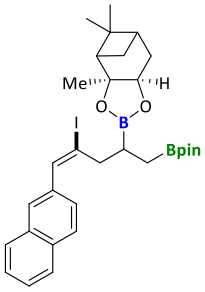
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.70 (s, 1H), 2.76 – 2.60 (m, 2H), 2.32 (s, 3H), 1.71 – 1.59 (m, 1H), 1.21 (s, 6H), 1.21 (s, 6H), 1.16 (s, 6H), 1.15 (s, 6H), 0.87 – 0.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.5, 134.0, 128.9, 128.8, 128.5, 83.1, 82.8, 36.8, 24.8, 24.8, 24.7, 24.7, 21.1.

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.7.

HRMS-(ESI+) for **$C_{24}H_{38}B_2ClO_4$ $[M+H]^+$:** calculated: 447.2639; found: 447.2652.

(3aS,7aR)-2-((*E*)-4-Iodo-5-(naphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-2-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (5.46)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (58 mg, 46%) as a mixture of two diastereoisomers (55:45).

Major product: **^{1}H NMR** (401 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.51 (s, 1H), 7.49 – 7.35 (m, 3H), 4.20 (d, J = 8.8 Hz, 1H), 2.80 (dtd, J = 13.2, 5.9, 1.4 Hz, 1H), 2.68 (m, 1H), 2.26 (m, 1H), 2.19 – 2.06 (m, 1H), 2.00 (td, J = 6.0, 5.5, 1.6 Hz, 1H), 1.87 – 1.74 (m, 2H), 1.69 (tt, J = 9.2, 5.5 Hz, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.06 (s, 6H), 1.02 (s, 6H), 0.94 – 0.87 (m, 2H), 0.81 (s, 3H).

Minor product: **^{1}H NMR** (401 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 4H), 7.51 (s, 1H), 7.49 – 7.35 (m, 3H), 4.20 (d, J = 8.8 Hz, 1H), 2.80 (dtd, J = 13.2, 5.9, 1.4 Hz, 1H), 2.68 (m, 1H), 2.26 (m, 1H), 2.19 – 2.06 (m, 1H), 2.00 (td, J = 6.0, 5.5, 1.6 Hz, 1H), 1.87 – 1.74 (m, 2H), 1.69 (tt, J = 9.2, 5.5 Hz, 1H), 1.34 (s, 3H), 1.25 (s, 3H), 1.08 (s, 6H), 1.06 (s, 6H), 0.94 – 0.87 (m, 2H), 0.81 (s, 3H).

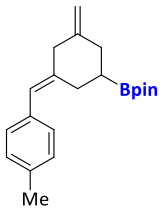
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.07, 132.82, 130.68, 129.71, 125.48, 125.24, 124.96, 124.79, 124.71, 124.09, 124.02, 123.54, 123.37, 109.90, 109.68, 83.05, 83.02, 80.30, 80.28, 75.16, 75.11, 48.72, 48.68, 38.88, 38.50, 36.83, 35.54, 32.78, 32.72, 26.02, 24.51, 23.83, 22.22, 22.12, 22.02, 21.42.

^{11}B NMR (129 MHz, $CDCl_3$) δ 34.85.

HRMS-(ESI+) for **$C_{31}H_{42}B_2IO_4$ [M+H]$^+$:** calculated: 627.2314; found: 627.2319.

- Characterisation of products of Pd-catalysed cross-coupling reaction and corresponding alcohols

(*E*)-4,4,5,5-Tetramethyl-2-(3-(4-methylbenzylidene)-5-methylenecyclohexyl)-1,3,2-dioxaborolane (5.31)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (58 mg, 89%) as a mixture of two diastereomers 3:1.

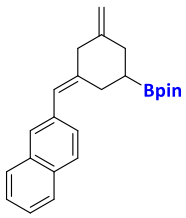
Major product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.17 – 7.06 (m, 4H), 6.19 (s, 1H), 4.64 (m, 2H), 2.95 (m, 2H), 2.89 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.42 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.33 (s, 3H), 2.20 – 2.13 (m, 2H), 2.09 (ddd, *J* = 14.0, 11.9, 1.7 Hz, 1H), 1.22 (s, 12H).

Minor product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.17 – 7.06 (m, 4H), 6.27 (m, 1H), 4.86 (m, 2H), 3.27 (m, 2H), 2.89 (dd, *J* = 14.0, 3.6 Hz, 1H), 2.42 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.33 (s, 3H), 2.20 – 2.13 (m, 2H), 2.09 (ddd, *J* = 14.0, 11.9, 1.7 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.9, 147.7, 141.2, 138.9, 137.5, 135.4, 135.4, 135.2, 135.2, 128.8, 128.7, 106.5, 83.1, 83.0, 46.1, 44.4, 38.8, 36.0, 29.4, 27.1, 24.7, 24.7, 24.7.

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

(*E*)-4,4,5,5-Tetramethyl-2-(3-methylene-5-(naphthalen-2-ylmethylene)cyclohexyl)-1,3,2-dioxaborolane (5.33)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (65 mg, 90%) as a mixture of two diastereomers 5:1.

Major product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83 – 7.73 (m, 4H), 7.49 – 7.32 (m, 3H), 6.37 (s, 1H), 4.68 (m, 2H), 3.01 (s, 2H), 2.93 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.45 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.28 – 2.17 (m, 1H), 1.24 (s, 2H), 1.20 (s, 12H).

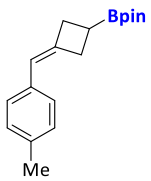
Minor product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83 – 7.73 (m, 4H), 7.49 – 7.32 (m, 3H), 6.47 (s, 1H), 4.94 – 4.86 (m, 2H), 3.34 (s, 2H), 2.93 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.45 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.28 – 2.17 (m, 3H), 1.24 (s, 6H), 1.24 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.8, 142.4, 135.7, 133.4, 131.8, 127.7, 127.5, 127.3, 127.3, 125.8, 125.3, 122.2, 106.7, 83.1, 46.2, 36.0, 29.6, 24.7, 24.7, 24.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.0.

HRMS-(ESI+) for **$C_{24}H_{30}BO_2$ [M+H]$^+$:** calculated: 361.2333; found: 361.2333.

4,4,5,5-Tetramethyl-2-(3-(4-methylbenzylidene)cyclobutyl)-1,3,2-dioxaborolane (5.35)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (51 mg, 90%).

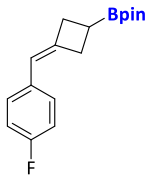
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (s, 4H), 6.02 (m, 1H), 3.21 – 3.04 (m, 2H), 3.04 – 2.86 (m, 2H), 2.31 (s, 3H), 2.11 – 2.00 (m, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 135.2, 135.2, 129.0, 127.0, 120.8, 83.2, 34.2, 33.7, 24.7, 24.7, 21.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.3.

HRMS-(ESI+) for **$C_{18}H_{26}BO_2$ [M+H]$^+$:** calculated: 285.2020; found: 285.2014.

2-(3-(4-Fluorobenzylidene)cyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.36)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (53 mg, 92%).

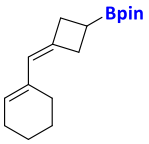
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.17 – 7.10 (m, 2H), 7.01 – 6.93 (m, 2H), 6.01 (m, 1H), 3.09 (m, 2H), 3.00 – 2.88 (m, 2H), 2.05 (m, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7 (d, $^{1}J_{C-F}$ = 246.0 Hz), 143.52, 136.76, 128.45 (d, $^{3}J_{C-F}$ = 7.9 Hz), 119.8, 115.12 (d, $^{2}J_{C-F}$ = 21.4 Hz), 83.2, 33.9, 33.7, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.0.

HRMS-(ESI+) for **$C_{17}H_{23}BFO_2$ [M+H]$^+$:** calculated: 289.1775; found: 289.1779.

2-(3-(Cyclohex-1-en-1-ylmethylene)cyclobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.37)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (39 mg, 72%).

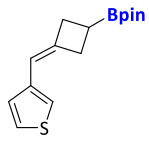
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.56 (m, 1H), 5.53 – 5.46 (m, 1H), 3.13 – 2.94 (m, 2H), 2.79 (m, 2H), 2.17 (m, 4H), 1.92 (m, 1H), 1.65 – 1.49 (m, 4H), 1.25 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 136.2, 125.4, 124.6, 83.1, 33.9, 33.4, 26.7, 25.6, 24.7, 24.7, 22.7, 22.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.9.

HRMS-(ESI+) for **$C_{17}H_{28}BO_2$ [M+H]$^+$:** calculated: 275.2182; found: 275.2187.

4,4,5,5-Tetramethyl-2-(3-(thiophen-3-ylmethylene)cyclobutyl)-1,3,2-dioxaborolane (5.38)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (49 mg, 89%).

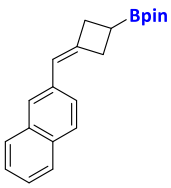
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (dd, J = 5.0, 2.9 Hz, 1H), 7.04 (dd, J = 5.0, 1.3 Hz, 1H), 6.96 (dd, J = 2.8, 1.2 Hz, 1H), 6.11 (m, 1H), 3.17 – 2.99 (m, 2H), 2.99 – 2.85 (m, 2H), 2.03 (m, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 139.4, 126.8, 125.0, 120.0, 115.6, 83.2, 33.7, 33.1, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5.

HRMS-(ESI+) for **$C_{15}H_{22}BO_2S$ [M+H]$^+$:** calculated: 277.1428; found: 277.1424.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-ylmethylene)cyclobutyl)-1,3,2-dioxaborolane (5.39)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (45 mg, 70%).

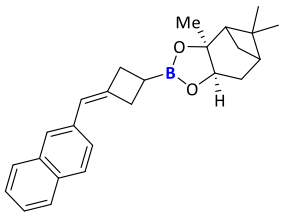
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.71 (m, 3H), 7.60 (s, 1H), 7.47 – 7.39 (m, 3H), 6.21 (m, 1H), 3.34 – 3.22 (m, 2H), 3.11 – 2.93 (m, 2H), 2.20 – 2.04 (m, 1H), 1.28 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 135.5, 133.6, 131.7, 127.7, 127.7, 127.5, 125.9, 125.7, 125.5, 125.2, 121.1, 83.3, 34.4, 34.0, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.4.

HRMS-(ESI+) for **$C_{21}H_{26}BO_2$ [M+H]$^+$:** calculated: 321.2025; found: 321.2028.

(3aS,7aR)-3a,5,5-Trimethyl-2-(3-(naphthalen-2-ylmethylene)cyclobutyl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole (5.47)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (64 mg, 86%).

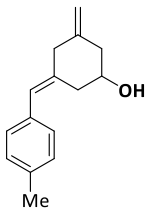
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 – 7.71 (m, 4H), 7.60 (d, J = 1.7 Hz, 1H), 7.41 (pd, J = 6.8, 1.5 Hz, 3H), 6.22 (p, J = 2.5 Hz, 1H), 4.31 (dd, J = 8.7, 1.8 Hz, 1H), 3.37 – 3.19 (m, 2H), 3.14 – 2.96 (m, 2H), 2.41 – 2.30 (m, 1H), 2.24 (dtt, J = 8.9, 5.8, 1.6 Hz, 1H), 2.17 – 2.11 (m, 1H), 2.08 (q, J = 5.3 Hz, 1H), 1.96 – 1.85 (m, 2H), 1.42 (s, 3H), 1.29 (d, J = 7.1 Hz, 3H), 1.16 (d, J = 10.9 Hz, 1H), 0.85 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.29, 133.00, 131.08, 129.22, 125.20, 125.16, 124.96, 123.37, 123.14, 123.01, 122.65, 118.61, 75.35, 48.73, 36.90, 35.61, 32.95, 32.05, 31.70, 26.09, 24.49, 23.90, 21.42.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.92.

HRMS-(ESI+) for **$C_{25}H_{30}BO_2$ $[M+H]^+$:** calculated: 373.2339; found: 373.2346.

(*Z*)-3-(4-Methylbenzylidene)-5-methylenecyclohexan-1-ol (5.32)



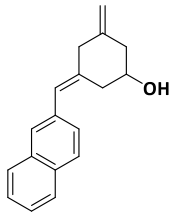
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/ethyl acetate (100:5). The product was isolated as a colorless oil (25 mg, 62%) as a mixture of two diastereomers 3:1.

Major product:**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.21 – 7.08 (m, 4H), 6.42 (s, 1H), 4.87 (s, 1H), 4.78 (s, 1H), 3.92 (s, 1H), 2.96 (s, 2H), 2.63 (d, *J* = 5.1 Hz, 2H), 2.56 (dd, *J* = 13.3, 3.7 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.33 (s, 3H).

Minor product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.21 – 7.08 (m, 4H), 6.33 (s, 1H), 5.05 (s, 1H), 4.99 (s, 1H), 3.92 (s, 1H), 2.96 (s, 2H), 2.63 (d, J = 5.1 Hz, 2H), 2.56 (dd, J = 13.3, 3.7 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.33 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.1, 135.9, 128.8, 128.7, 128.1, 126.1, 111.0, 68.8, 45.5, 43.2, 36.8, 21.1.

(*Z*)-3-Methylene-5-(naphthalen-2-ylmethylene)cyclohexan-1-ol (5.34)

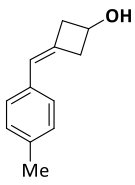


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/ethyl acetate (100:5). The product was isolated as a colorless oil (26 mg, 51%) as a mixture of two diastereomers 5:1.

Major product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83 – 7.75 (m, 4H), 7.68 (d, J = 1.5 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.37 (dd, J = 8.5, 1.7 Hz, 1H), 6.60 (d, J = 1.8 Hz, 1H), 4.94 – 4.89 (m, 1H), 4.82 (dt, J = 2.2, 1.2 Hz, 1H), 3.96 (s, 1H), 3.03 (dq, J = 2.7, 1.3 Hz, 2H), 2.75 – 2.69 (m, 2H), 2.64 – 2.55 (m, 1H), 2.43 – 2.33 (m, 1H). Minor product: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83 – 7.75 (m, 4H), 7.68 (d, J = 1.5 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.37 (dd, J = 8.5, 1.7 Hz, 1H), 6.57 (d, J = 1.4 Hz, 1H), 5.08 (s, 1H), 5.01 (d, J = 6.6 Hz, 1H), 3.96 (s, 1H), 3.03 (dq, J = 2.7, 1.3 Hz, 2H), 2.75 – 2.69 (m, 2H), 2.64 – 2.55 (m, 1H), 2.43 – 2.33 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 137.1, 134.9, 133.9, 132.1, 132.1, 132.0, 131.9, 131.9, 128.5, 128.4, 111.2, 68.8, 45.6, 43.2, 36.9.

3-(4-Methylbenzylidene)cyclobutan-1-ol (5.40)

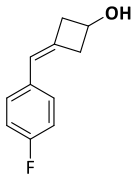


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl acetate (100:50). The product was isolated as a colorless oil (34 mg, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 – 7.05 (m, 4H), 6.21 (m, 1H), 4.55 – 4.43 (m, 1H), 3.31 (ddtd, J = 16.3, 7.0, 3.7, 2.3 Hz, 1H), 3.15 (ddtd, J = 15.9, 7.1, 3.7, 1.7 Hz, 1H), 2.97 (ddt, J = 16.1, 6.3, 3.1 Hz, 1H), 2.85 (ddt, J = 15.8, 6.1, 2.9 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.07, 129.09, 127.00, 122.49, 64.65, 43.88, 43.33, 21.14.

3-(4-Fluorobenzylidene)cyclobutan-1-ol (5.41)

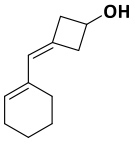


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl acetate (100:50). The product was isolated as a colorless oil (35 mg, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (m, 2H), 7.03 – 6.94 (m, 2H), 6.20 (s, 1H), 4.56 – 4.45 (m, 1H), 3.32 – 3.23 (m, 1H), 3.20 – 3.11 (m, 1H), 3.00 – 2.91 (m, 1H), 2.91 – 2.79 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7 (d, $^{1}J_{C-F}$ = 247.3 Hz), 139.5, 128.5 (d, $^{3}J_{C-F}$ = 7.7 Hz), 121.5, 115.26 (d, $^{2}J_{C-F}$ = 21.6 Hz), 64.5, 43.8, 43.1

3-(Cyclohex-1-en-1-ylmethylene)cyclobutan-1-ol (5.42)

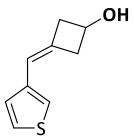


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl acetate (100:50). The product was isolated as a colorless oil (32 mg, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 (s, 1H), 5.55 (d, J = 4.5 Hz, 1H), 4.41 (m, 1H), 3.33 – 3.21 (d, J = 16.2 Hz, 1H), 3.00 (d, J = 16.7 Hz, 1H), 2.83 (d, J = 16.4 Hz, 1H), 2.70 (d, J = 16.2 Hz, 1H), 2.21 – 2.04 (m, 4H), 1.72 – 1.49 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 129.5, 126.5, 126.2, 64.3, 43.6, 43.2, 26.6, 25.6, 22.7, 22.2.

3-(Thiophen-3-ylmethylene)cyclobutan-1-ol (5.43)

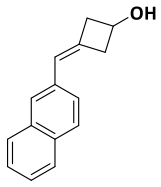


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl acetate (100:50). The product was isolated as a colorless oil (33 mg, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (d, J = 2.9 Hz, 1H), 7.12 – 6.98 (m, 2H), 6.28 (m, 1H), 4.50 (dd, J = 7.0, 6.0 Hz, 1H), 3.29 (ddd, J = 16.3, 7.1, 3.6, Hz, 1H), 3.14 (ddd, J = 16.0, 7.1, 3.6, Hz, 1H), 3.00 – 2.77 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 133.1, 126.6, 125.3, 120.6, 117.2, 64.2, 43.3, 43.0.

3-(Naphthalen-2-ylmethylene)cyclobutan-1-ol (5.44)



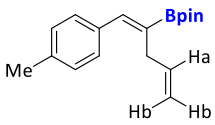
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl acetate (100:50). The product was isolated as a colorless oil (42 mg, 99%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.72 (m, 3H), 7.60 (s, 1H), 7.47 – 7.36 (m, 3H), 6.40 (m, 1H), 4.54 (tt, J = 7.0, 6.1 Hz, 1H), 3.49 – 3.37 (m, 1H), 3.28 – 3.15 (m, 1H), 3.10 (ddd, J = 16.3, 6.2, 3.2 Hz, 1H), 2.92 (ddd, J = 15.9, 6.0, 2.9 Hz, 1H).

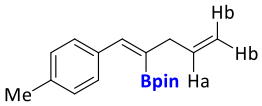
^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.7, 132.3, 131.0, 129.4, 125.3, 125.2, 125.0, 123.5, 123.2, 122.9, 122.8, 120.2, 62.0, 41.5, 40.9.

- Characterisation of borylcupration of a (*Z*):(*E*) = 2:1 ratio mixture of 5.1a, and subsequent 1,3-B/Cu shift - protonation towards 5.2-(*Z*):5.2-(*E*) within the same 2:1 ratio.

4,4,5,5-tetramethyl-2-(1-(p-tolyl)penta-1,4-dien-2-yl)-1,3,2-dioxaborolane (5.1a (*Z*):(*E*) = 2:1)



(Z)-**5.1a**



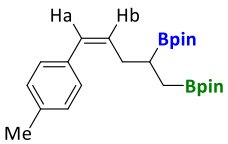
(E)-**5.1a**

The products were purified by flash chromatography using as eluent a mixture of pentane/Et_2O (300:1). The products were isolated as a mixture of isomers 2:1.

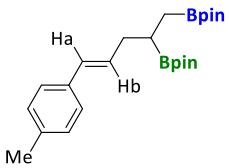
(*Z*)-5.1a ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (s, 1H), 7.28 – 7.24 (m, 2H), 7.19 – 7.11 (m, 2H), 6.10 – 5.96 (m, 1H), 5.16 – 4.95 (m, 2H), 3.13 (dd, J = 5.7, 1.5 Hz, 2H), 2.34 (s, 3H), 1.30 (s, 12H).

(*E*)-5.1a ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (s, 1H), 7.24 – 7.20 (m, 2H), 7.09 – 7.06 (m, 2H), 5.94 – 5.80 (m, 1H), 5.11 – 4.98 (m, 2H), 3.05 (dd, J = 6.7, 1.5 Hz, 2H), 2.33 (s, 3H), 1.26 (s, 12H).

2,2'-(5-(p-Tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.2a (*Z*):(*E*) = 2:1)



(Z)-**5.2a**



(E)-**5.2a**

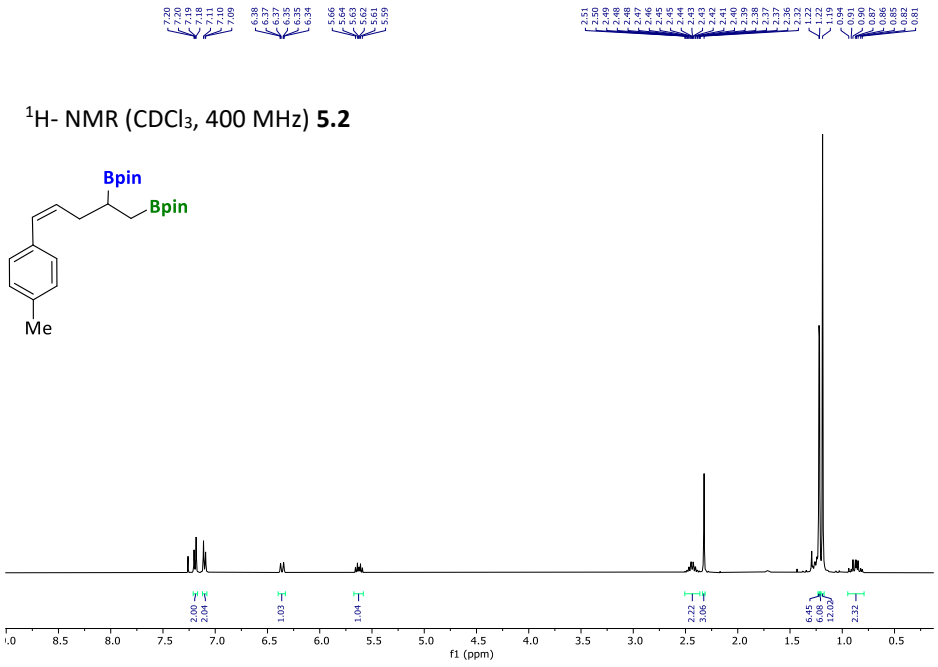
The products were purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The products were isolated as a mixture of isomers 2:1.

(*Z*)-5.2a ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.36 (dd, J = 11.7, 2.0 Hz, 1H), 5.62 (dt, J = 11.7, 7.3 Hz, 7.3 Hz, 1H), 2.44 (m, 2H), 2.32 (s, 3H), 1.23 (s, 6H) 1.22 (s, 6H), 1.21 (m, 1H), 1.19 (s, 12H), 0.95 – 0.79 (m, 2H).

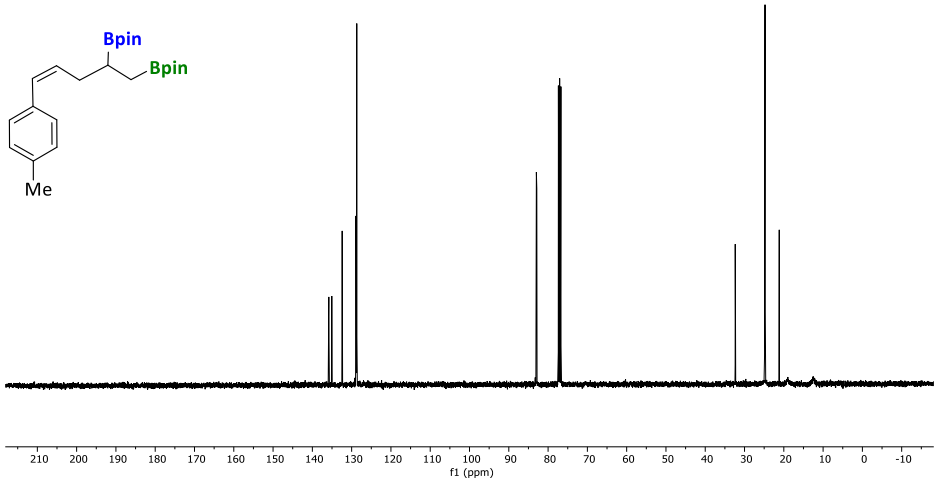
(*E*)-5.2a ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.34 (dd, J = 11.7, 2.0 Hz, 1H), 6.16 (dt, J=15.8 Hz, 7 Hz, 7 Hz, 1H), 2.44 (m, 2H), 2.32 (s, 3H), 1.22 (s, 12H), 1.21 (m, 1H), 1.19 (s, 12H), 0.95 – 0.79 (m, 2H).

- Selected NMR spectra

^{1}H- NMR ($CDCl_3$, 400 MHz) **5.2**

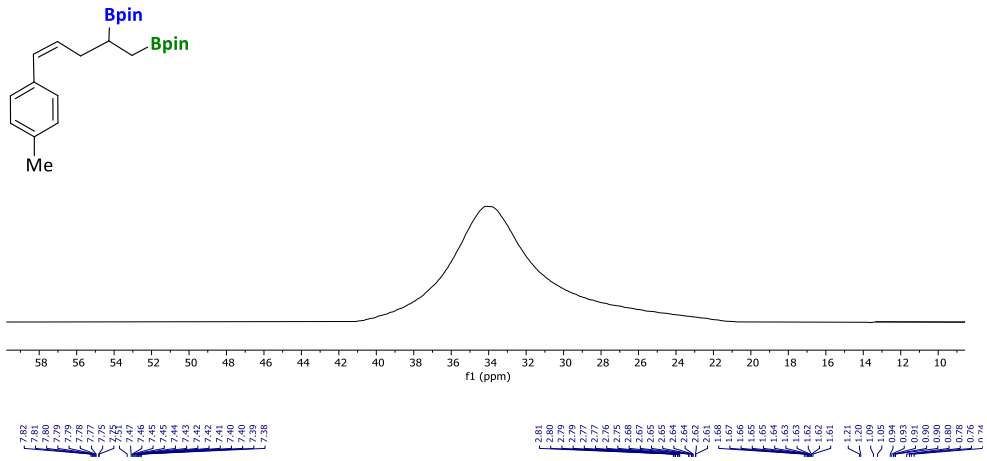


^{13}C- NMR ($CDCl_3$, 100 MHz) **5.2**

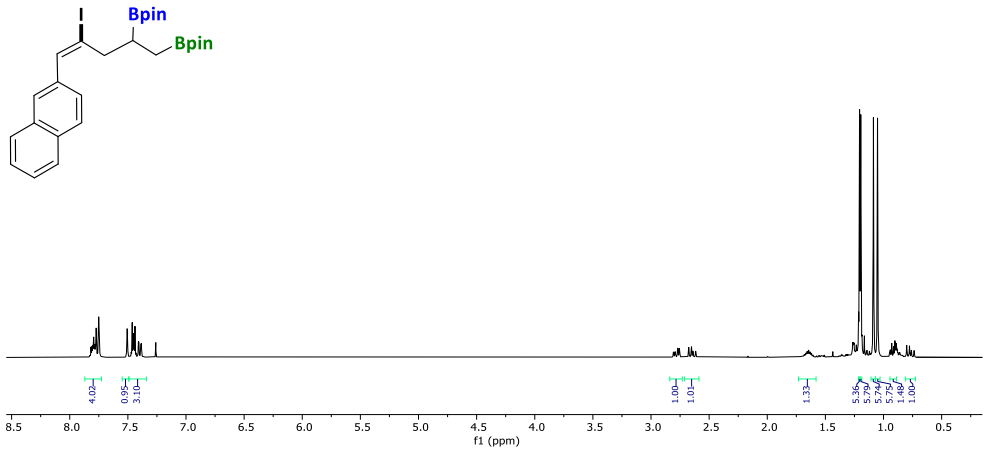


34.13

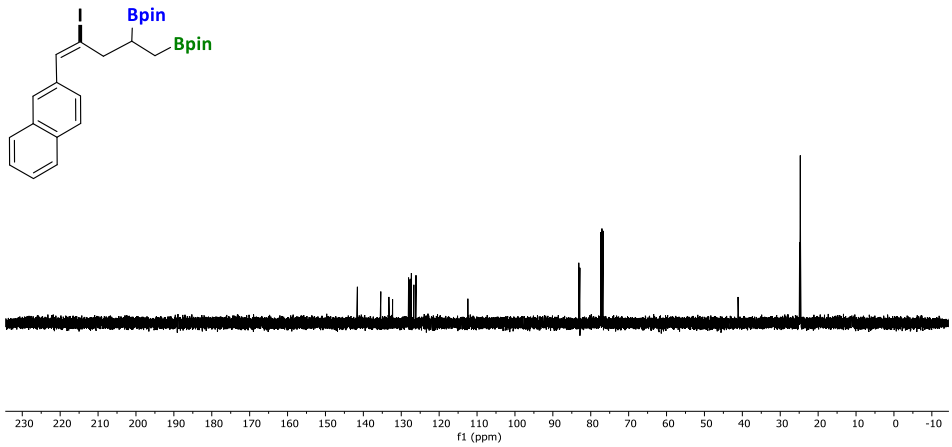
^{11}B- NMR ($CDCl_3$, 128.3 MHz) **5.2**



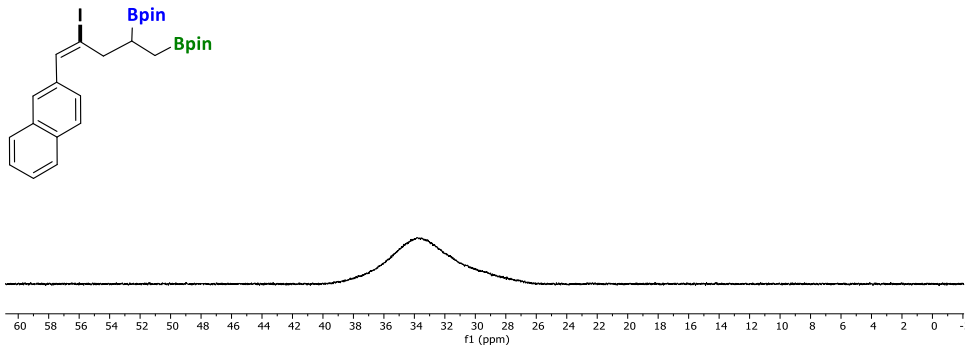
^{1}H- NMR ($CDCl_3$, 400 MHz) **5.28**



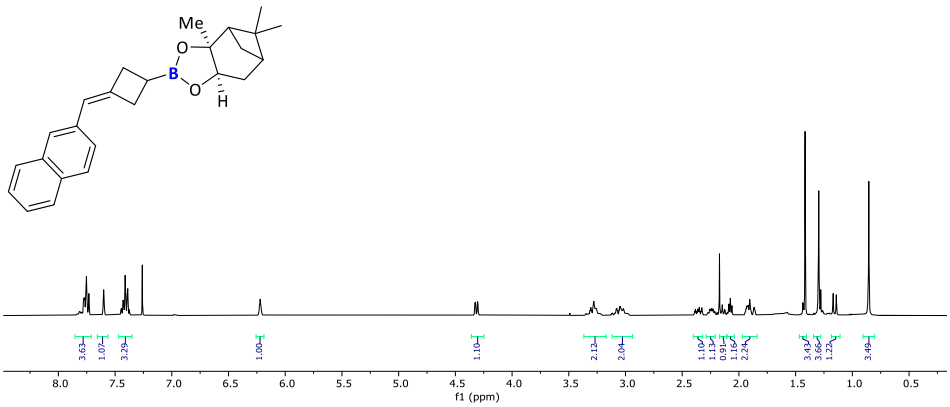
^{13}C- NMR ($CDCl_3$, 100 MHz) **5.28**



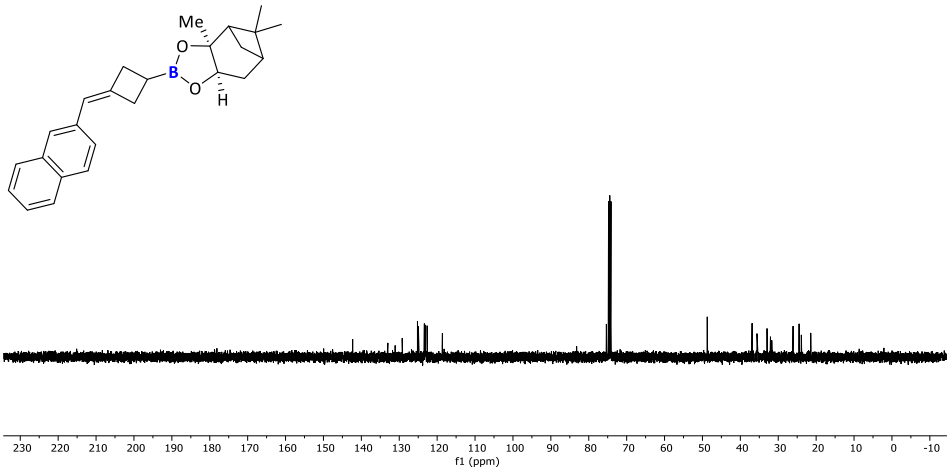
^{11}B- NMR ($CDCl_3$, 128.3 MHz) **5.28**



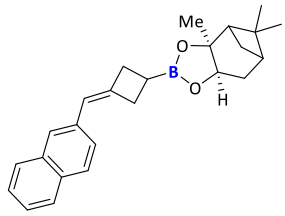
^{1}H- NMR ($CDCl_3$, 400 MHz) **5.47**

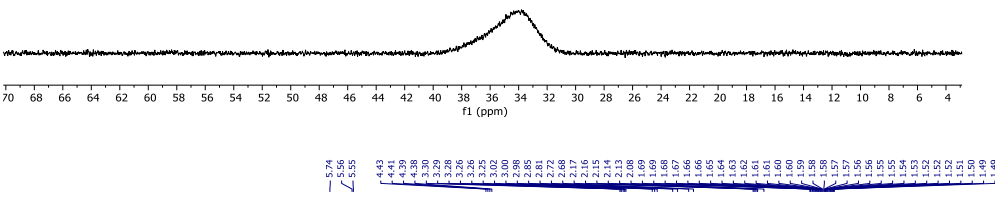


^{13}C- NMR ($CDCl_3$, 100 MHz) **5.47**

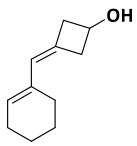


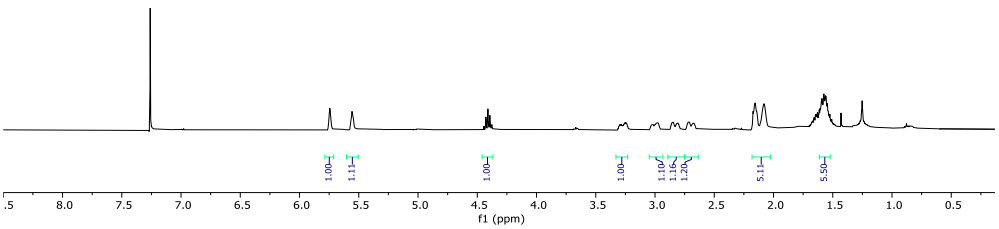
^{11}B- NMR ($CDCl_3$, 128.3 MHz) **5.47**

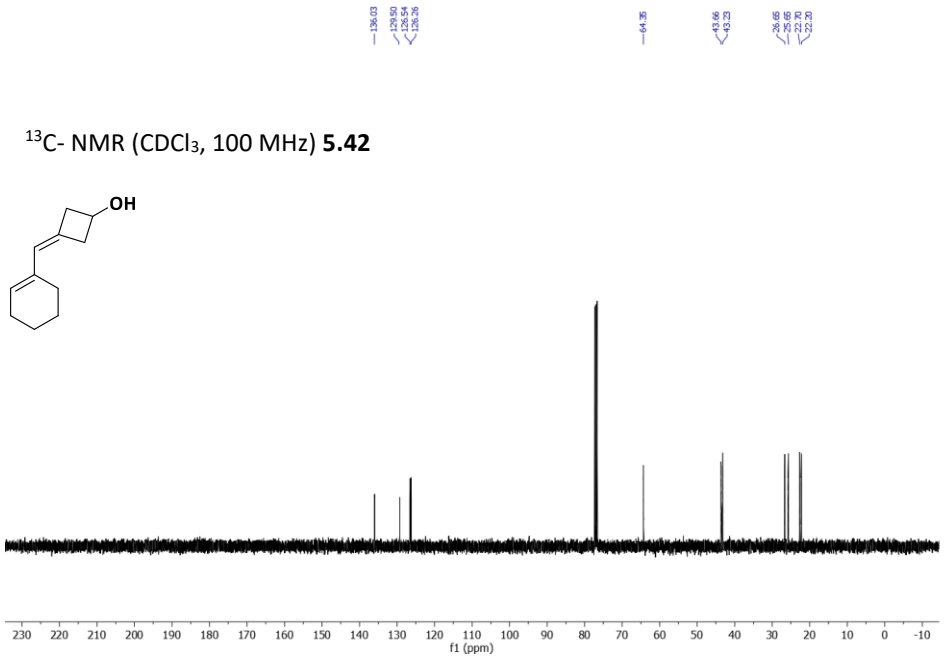




^{1}H- NMR ($CDCl_3$, 400 MHz) **5.42**







^{13}C- NMR ($CDCl_3$, 100 MHz) **5.42**

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[24] Calculations were performed with Gaussian16 using ωB97X-D functional. The basis set was 6-31g(d,p) for B, C, O and H atoms; and lanl2dz pseudopotentials supplemented with f and d shells for Cu, P, and K. Free-energies were computed at a

concentration of 1 M and a temperature of 298.15 K. The solvent effect of THF (ε=7.4257) was evaluated by SMD continuum solvent model. The bond orders and the atomic charges were determined with NBO method. See the Supporting Information for details.

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CHAPTER VI

Alkenylboranes for 1,4-boron-copper migration

UNIVERSITAT ROVIRA I VIRGILI
Contributions to Precise Skeletal Editing via Alkenylboranes
Paula Dominguez Molano

6.1. State of the art: precedents of copper 1,4-migration reaction

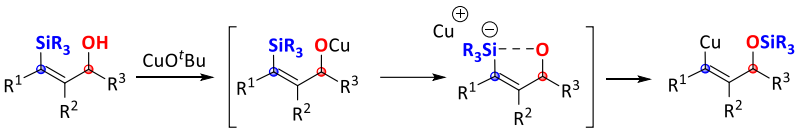
The 1,4-migration facilitated by transition metals has unveiled an unexpected method for translocating several atoms along molecular structures. The primary complexes involved in 1,4-metal rearrangements include Rh and Pd.[1] However, other metals such as Ni,[2] Co,[3] and Ir[4] have also demonstrated some capacity for participating in remote atom 1,4-migration. On the other hand, Cu complexes are less commonly employed for atom relocation, and heteroatoms have been necessary, in some cases, to assist in the process.

Copper (I) has been utilised for the 1,4-C(sp^2)-to-O silyl migration through hypercoordinated cyclic silicates in (*Z*)-γ-trimethylsilyl allylic alcohol, facilitating the Brook-type rearrangement through transmetallation reaction, as described by Takeda and co-workers (Scheme 6.1a).[5] Additionally, the authors reported that vinyl copper species underwent electrophilic trapping, in the absence of palladium catalyst, to afford the cross-coupling product with complete retention of configuration.

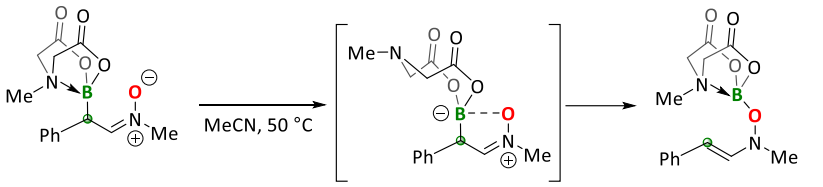
Similarly, Yudin and co-workers reported a neighbouring atom-promoted 1,4-boryl shift reaction using tetracoordinated MIDA (MIDA = *N*-methyliminodiacetic acid) boryl moiety, in which boron migrates as an electrophile in its pseudo-tricoordinate form.[6] In this case, hypercoordinated cyclic boronic esters have been proposed as key intermediates in the 1,4-boryl migration, forming a five-membered zwitterionic intermediate that evolves to O-boryl hydroxylamine (Scheme 6.1b).

In both studies, the assistance of oxygen appeared to be crucial for the successful 1,4-silyl or 1,4-boryl migration, favouring the formation of five-membered ring intermediates with hypercoordinated Si and B atoms, respectively.

a) *1,4-C(sp^2)-to-O Silyl Migration*



b) *1,4-C(sp^3)-to-O Boryl Migration*



O-boryl hydroxylamine

Scheme 6.1. Precedents of a) 1,4-Si and b) 1,4-B migration sequences.

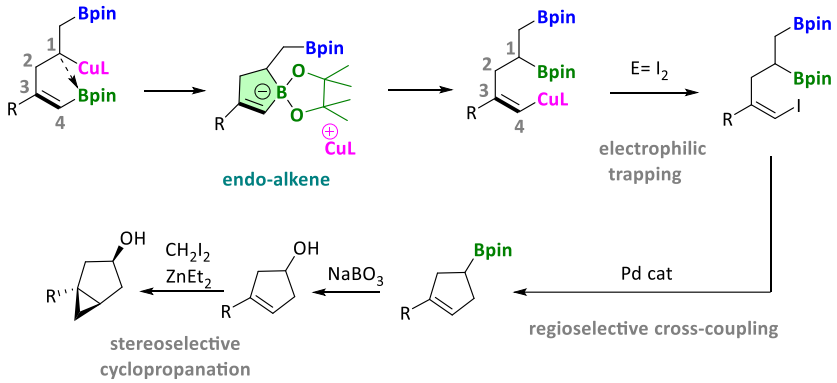
6.2. Project aims

In this project, we pursued a novel concept based on 1,4-boryl copper shift that occurs without the aid of a heteroatom. Our main objective is the development of a remote 1,4-carbon-to-carbon boryl migration triggered by the nucleophilic attack of a copper-alkyl moiety (Cu-C(sp^3)) on the vacant *p* orbital of a boron atom bonded to a C(sp^2) carbon. This results in a hypercoordinated boracycle structure, facilitating the remote Cu/B shift (Scheme 6.2).

The specific objectives are:

- Viability of 1,4-boryl copper shift in comparison with our previously observed 1,3-boryl copper shift.[7]
- Investigation about how the alkene disposition influences the reaction.
- Application of this new conceptual methodology to construct a platform for a stereoselective bicyclic synthesis.

New Concept: copper catalysed 1,4-Csp^2-to-Csp^3 Boryl Migration



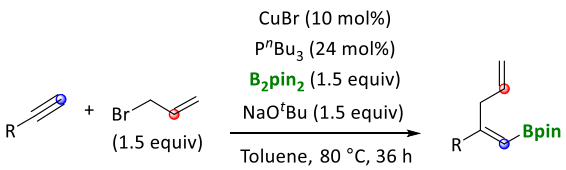
Scheme 6.2. Proposed project aims for the 1,4-boron/copper rearrangement reaction of borylated skipped dienes.

6.3. Results and discussion

6.3.1. Synthesis of borylated skipped (*E*)-dienes

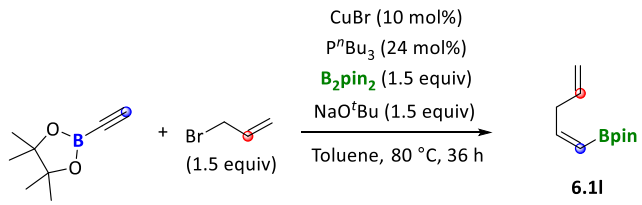
To investigate the 1,4-B/Cu shift reaction, we first synthesised (*E*)-trisubstituted vinyl pinacol boronic esters with a 1,4-diene skeleton as model substrates. We adopted the method by Zhao, Wang, and co-workers,[8] which reported an efficient copper-catalysed regioselective formal allylboration of terminal alkynes with B_2pin_2 (bis(pinacolato)diboron). We successfully reproduced the synthesis for substrates **6.1a**-**6.1i,** and prepared compounds **6.1j** and **6.1k** for the first time, demonstrating that the reaction is compatible with alkenyl and silyl groups (Scheme 6.3a). Unexpectedly, when 2-ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane reacted with CuBr/P^{n}Bu$_3$ in the formal allylboration reaction, the product **6.1l** was formed, indicating that original pinacolboryl moiety was removed, suggesting a protodeborylation pathway (Scheme 6.3b).

a)



6.1a R=C_6H_5
6.1b R=*p*Me-C_6H_4
6.1c R=*p*OMe-C_6H_4
6.1d R=*p*Cl-C_6H_4
6.1e R=*p*F-C_6H_4
6.1f R=*o*Me-C_6H_4
6.1g R=*o*Br-C_6H_4
6.1h R=2-naphthyl
6.1i R=3-thienyl
6.1j R=1-cyclohexenyl
6.1k R=trimethylsilyl

b)



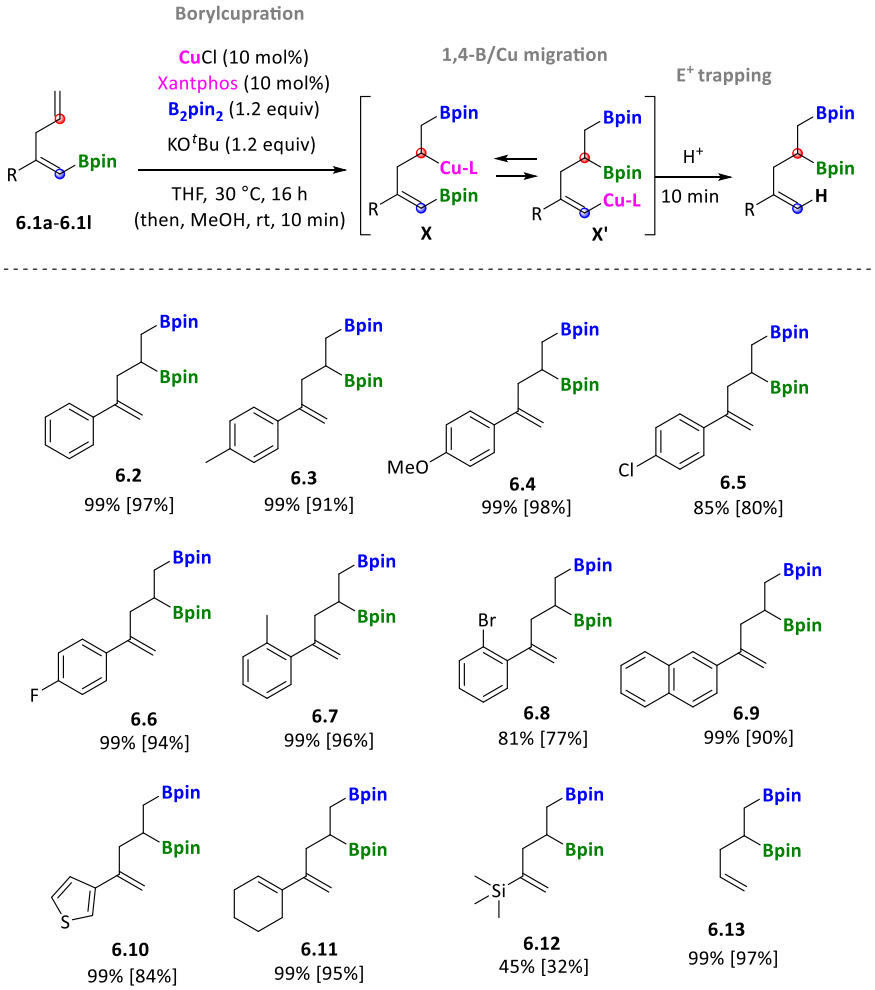
6.1l

Scheme 6.3. Synthesis of borylated skipped dienes.

6.3.2. Substrate scope of boron-copper 1,4-rearrangement

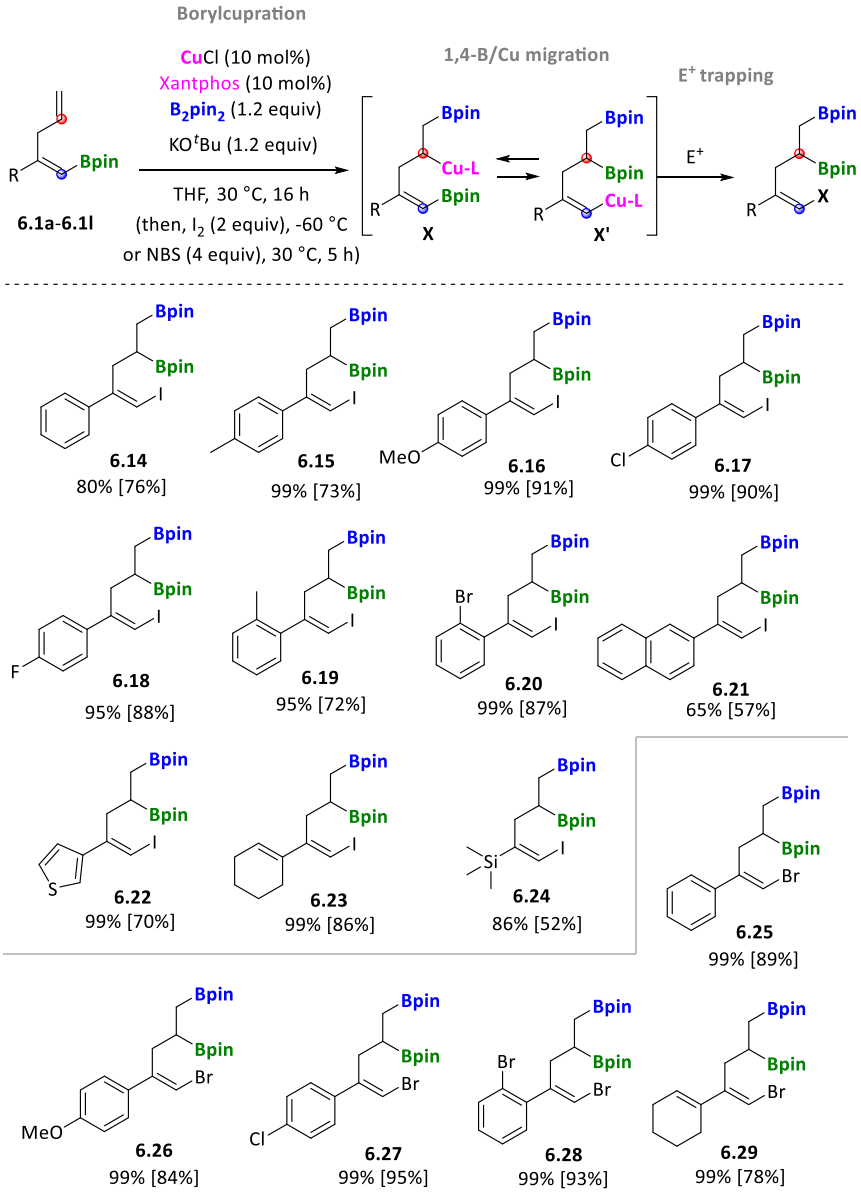
Having previously synthesised the substrates, we proceeded to explore the borylcupration of borylated skipped (*E*)-dienes using the highly efficient CuCl/Xantphos catalytic system for regioselective borylcupration reaction.[9-11] The conversion of model substrate **6.1a** into diborated alkene **6.2** was achieved quantitatively using 10 mol% of CuCl/Xantphos, 1.2 equivalents of B_2pin_2 and KO^tBu as the base, at 30 °C in THF (Scheme 6.4). The product **6.2** was formed via Cu-catalysed regioselective borylcupration on the terminal alkene of **6.1a**, producing the organocopper species **X**. This species then underwent a straightforward intramolecular 1,4-B/Cu shift, forming the alkenyl copper intermediate **X'**, which was subsequently trapped with a proton through the subsequent work-up by the addition of methanol.

This reaction demonstrated general applicability to substrates with both electron-withdrawing and electron-donating aryl substituents in *para* and *ortho* positions (Scheme 6.4, products **6.3**-**6.8**). It also exhibited notable functional group tolerance, successfully accommodating 2-naphthyl and 3-thienyl groups (Scheme 6.4, products **6.9**-**6.10**). Introducing a cyclohexenyl group into substrate **6.1j** we addressed the chemoselectivity issue during initial borylcupration. Interestingly, under the catalytic optimised reaction conditions, the borylcupration took place selectively on the terminal alkene, yielding the desired diborated product **6.11** in 95% isolated yield. The compatibility of the trimethylsilyl group in the Cu-catalysed 1,4-boryl migration was critical for generating product **6.12**, as no 1,3-C(sp^2)-to-C(sp^3) silyl migration occurred, consistent with the higher hypercoordination ability of the boryl group compared to the silyl group. Finally, the unsubstituted substrate (*Z*)-4,4,5,5-tetramethyl-2-(penta-1,4-dien-1-yl)-1,3,2-dioxaborolane (**6.1l**) was efficiently transformed into the diborated product **6.13** in high yield (Scheme 6.4).



Scheme 6.4. Substrate scope for the 1,4-boron/copper rearrangement followed by protonation reaction. Yields determined by NMR spectroscopy using naphthalene as internal standard. Isolated yields are shown in brackets.

After evaluating the viability of combining the selective borylcupration with 1,4-B/Cu shift and protonation, in a single operation, we explored the complementary I_2-iodonolysis[12] of the alkenyl copper (I) intermediates **X'**. This process yielded the key vinylic iodide products **6.14**-**6.24** in high yields (Scheme 6.5). Alternatively, stereospecific electrophilic trapping with NBS (*N*-bromosuccinimide) efficiently generated the brominated trisubstituted alkenes **6.25**-**6.29** (Scheme 6.5).



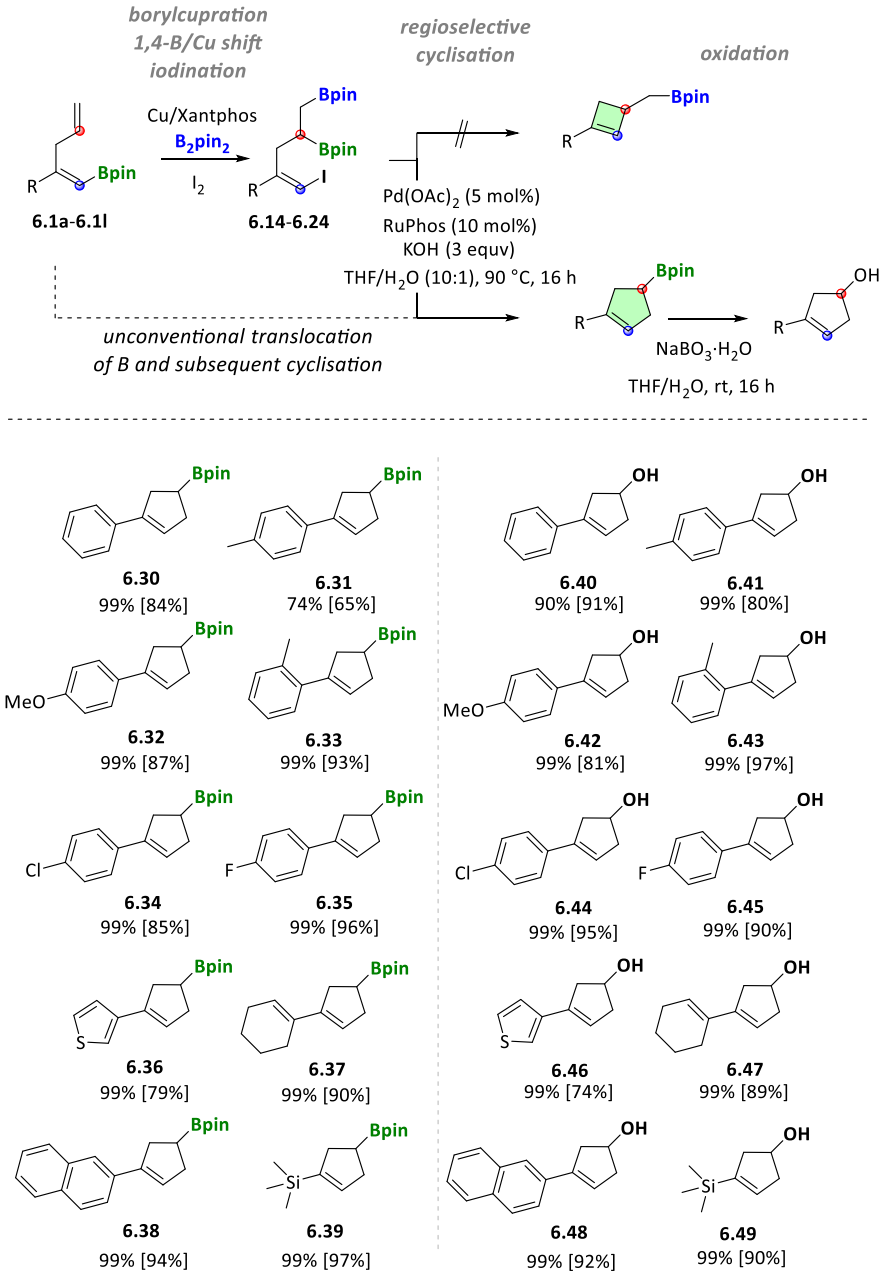
Scheme 6.5. Substrate scope for the 1,4-boron/copper rearrangement followed by electrophilic trapping of I_2 or NBS. Yields determined by NMR spectroscopy using naphthalene as internal standard. Isolated yields are shown in brackets.

6.3.3. Synthetic applications via palladium-catalysed cross-coupling reaction

The synthetic application of novel diborated iodoalkenyl products **6.14**-**6.24** was developed to prepare functionalised borylated cyclopentenes via a palladium-catalysed regioselective cross-coupling sequence. When compound **6.14** reacted with $Pd(OAc)_2$/RuPhos,[13] a regioselective cyclisation with the terminal pinacolboryl moiety occurred, exclusively generating the cyclopentene structure **6.30**, while retaining the original Bpin moiety from substrate **6.1a** (Scheme 6.6). This sequence demonstrated an unconventional remote translocation of boron along boracycle intermediates, which are cycled into valuable functionalised cyclopentenes.[14]

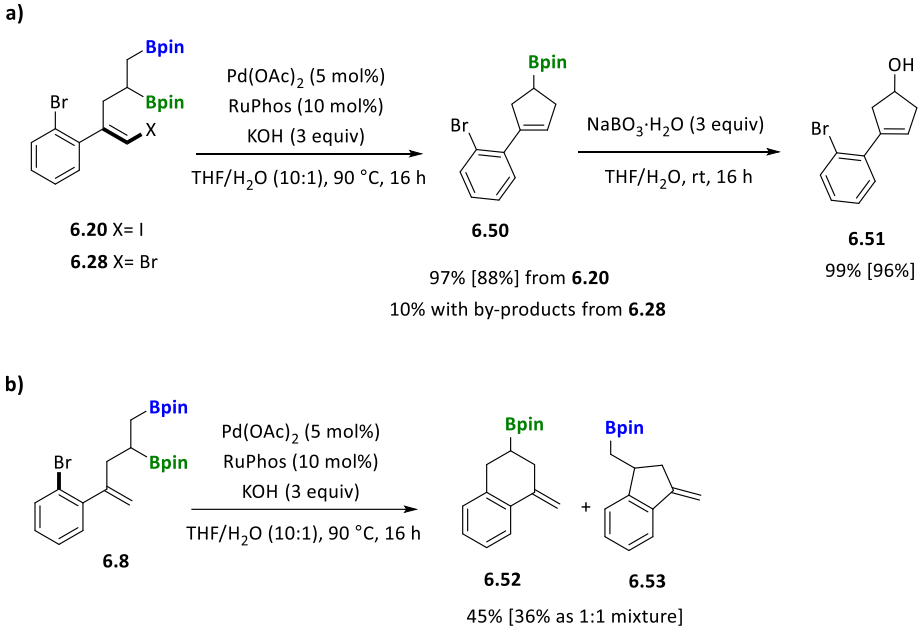
In this context, the reaction was compatible with both electron-donating and electron-withdrawing substituents in the *para* and *ortho* positions of the aryl group (Scheme 6.6, products **6.31**-**6.35**), as well as 3-thienyl, cyclohexenyl, and 2-naphthyl groups (Scheme 6.6, products **6.36**-**6.38**). Notably, the trimethylsilyl-substituted (*E*)-iodinated alkene **6.24** was efficiently transformed into the corresponding borylated/silylated cyclopentene **6.39**, with an isolated yield of 97%.

In addition, the oxidation of the C–B bond in these borylated functionalised cyclopentenes provided facile access to aryl- or vinyl-substituted cyclopentenyl alcohols **6.40**-**6.49**, which were otherwise challenging to synthesise via Cu-catalysed arylation of cyclopentenes with diaryliodonium salts (Scheme 6.6).[15] These 3-arylcyclopent-3-en-1-ol products were crucial in the synthesis of a prostaglandin endoperoxide model system.[16]



Scheme 6.6. Regioselective Pd-cyclisation towards cyclopentene synthesis and oxidation to aryl- or vinyl-substituted cyclopentenyl alcohols. Yields determined by NMR spectroscopy using naphthalene as internal standard. Isolated yields are shown in brackets.

We explored the competitive regioselective intramolecular cross-coupling reaction of diborylated (*E*)-iodo substituted alkene **6.20**, which could potentially yield four different cyclic compounds. Gratifyingly, the reaction was regioselective, exclusively producing and isolating cyclopentene structure **6.50**. The Bpin moiety from the original substrate **6.1g** remained intact, and the *ortho*-Br-C_6H_4 bond was unaltered (Scheme 6.7a). In this context, oxidation of product **6.50** resulted in the valuable functionalised cyclopentenol **6.51** with high yield (Scheme 6.7a). To gain further insight into the exclusive formation of cyclopentene **6.50**, we conducted the intramolecular cross-coupling reaction with the analogous compound **6.28**, which contains two C(sp^2)–Br bonds. Surprisingly, cyclopentene **6.50** was only detected in about 10% yield, accompanied by other by-products (Scheme 6.7a). This confirmed the crucial role of C(sp^2)–I in this competitive intramolecular coupling. As expected, the oxidative addition of C(sp^2)–I to the Pd complex was favoured over the oxidative addition of C(sp^2)–Br. In addition, when product **6.8** was submitted to the intramolecular cross-coupling reaction conditions, an equative mixture of substituted tetrahydro naphthalene **6.52** and dihydro indene **6.53** were isolated in a 1:1 ratio (Scheme 6.7b).



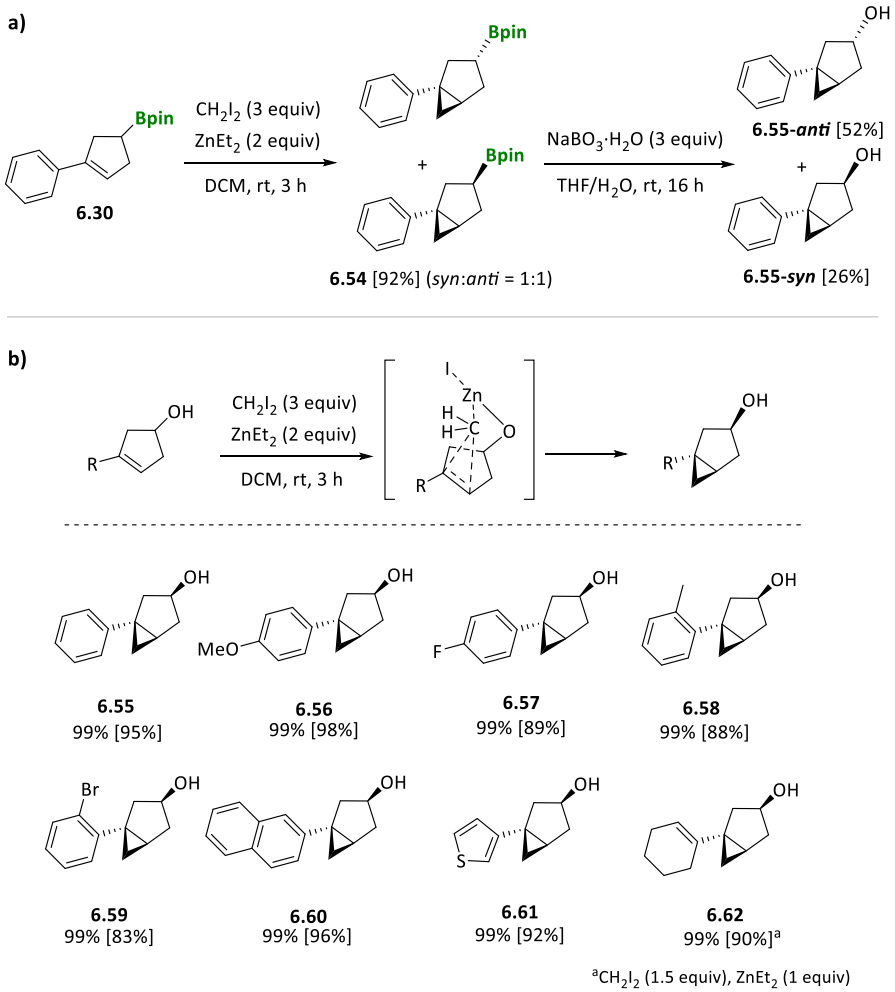
Scheme 6.7. Comparative regioselective intramolecular competitive cross-coupling reactions. Yields determined by NMR spectroscopy using naphthalene as internal standard. Isolated yields are shown in brackets.

6.3.4. Stereoselective synthesis of bicycles via Simmons-Smith cyclopropanation reaction

Subsequently, we performed the Simmons-Smith cyclopropanation of borylated cyclopentene **6.30** to develop a convenient platform for constructing bicyclic systems, which are considered analogues of Thujone, well-known inhibitors of the γ-aminobutyric acid A receptor.[17] Using Furukawa conditions,[18] the reaction yielded the borylated bicyclic compound **6.54** in quantitative yield as a 1:1 mixture of both diastereoisomers. Oxidation of **6.54** with $NaBO_3·H_2O$ proceeded smoothly, resulting in the isolation of both corresponding alcohols **6.55-*syn*** and **6.55-*anti*** (Scheme 6.8a).

However, when substituted cyclopentenyl alcohol **6.40** was reacted with diiodomethane and the zinc complex, the cyclopropanation proceeded diastereoselectively. This stereoselectivity might be due to zinc coordinating with the alcohol substituent, directing the cyclopropanation to occur *cis* to the hydroxyl group. Following this strategy, compound **6.55** was isolated in a 95% yield, as a single diastereomer (Scheme 6.8b).

The methodology was extended to include aryl groups with electron-donating and electron-withdrawing substituents in the *para* and *ortho* positions (Scheme 6.8b, products **6.56**-**6.59**), as well as 2-naphthyl and 3-thienyl groups (Scheme 6.8b, products **6.60**-**6.61**). Notably, when substituted cyclohexenyl cyclopentenyl alcohol **6.47** reacted with CH_2I_2 (3 equiv) and $ZnEt_2$ (2 equiv), both alkene groups underwent cyclopropanation, yielding mixtures of the two diastereoisomers. However, lowering the reagent loading to CH_2I_2 (1.5 equiv) and $ZnEt_2$ (1 equiv), compound **6.47** was selectively converted into product **6.62**, where only the double bond from the cyclopentenyl alcohol fragment was cyclopropanated in a stereoselective manner, as expected (Scheme 6.8b).



Scheme 6.8. Stereoselective synthesis of bicycles via Simmons-Smith cyclopropanation reaction. Yields determined by NMR spectroscopy using naphthalene as internal standard. Isolated yields are shown in brackets.

6.4. Computational studies (carried out by Prof. Carbó)

DFT calculations were performed by Dr. Albert Solé Daura and Prof. Jorge J. Carbó to elucidate the reaction mechanism of the stereospecific borylcupration – 1,4-B/Cu shift of borylated skipped (*E*)-dienes, and compared them with our previous investigations on the 1,3-B/Cu migration of the Bpin moiety from C(sp^2) to C(sp^3).[7,19]

Figure 6.1 illustrated the calculated free-energy profile for the borylcupration mechanism of substrate **6.1a** with B_2pin_2, catalysed by the Cu(I)-Xantphos complex in the presence of KO^{t}Bu, followed by sequential electrophilic trapping with I_2. The initial phase of the mechanism involved (1) the *in situ* formation of the active catalyst Xantphos-Cu(O^{t}Bu) complex **I1**, (2) σ-bond metathesis with B_2pin_2 to produce the Xantphos-Cu-boryl species **I2**, (3) coordination of substrate **6.1a** to the Cu complex through the terminal double bond, resulting in adduct **I3**, and (4) regioselective borylcupration of the terminal double bond to generate the alkyl-Cu(I) complex **I4**, with the Bpin group regioselectively attached to the terminal carbon. These steps were well-documented and have been deeply studied computationally for similar processes and substrates.[7,11]

Subsequently, the alkyl-copper(I) intermediate **I4** could undergo the unprecedented 1,4-B/Cu shift from remote C(sp^2)–Bpin to C(sp^3)–Cu position along the alkyl fragment.

The 1,4-migration occurred in two steps (Figure 6.1). First, the Cu-alkyl moiety nucleophilically attacked the boron atom of the C(sp^2)–Bpin fragment. This attack proceeded via a 5-membered ring transition state. The resulting intermediate **I5** featured the 5-membered boracycle substrate bonded to copper through a pinacol oxygen atom.

From **I5**, the reaction could proceed via two possible pathways: (i) the migration of the Bpin moiety to the C(sp^3) position accompanied by boracycle ring opening through the cleavage of the B–C(sp^2) bond, forming the Cu-alkenyl complex **I6**, which could then undergo transmetallation with the KO^{t}Bu base (dashed lines in Figure 6.1); or (ii) direct transmetallation of the KO^{t}Bu base complex with the Cu-boracyclic complex **I5**. In both pathways, the Cu-O^{t}Bu catalyst complex was regenerated, and the resulting product was a 5-membered boracycle stabilised by a K^+ counterion.

Finally, the 1,4 migration was completed by the electrophilic trapping of boracycle **I7** with I_2, yielding the vinylic iodide product **6.14**. This final step, which was highly exergonic, provided the thermodynamic driving force for the reaction.

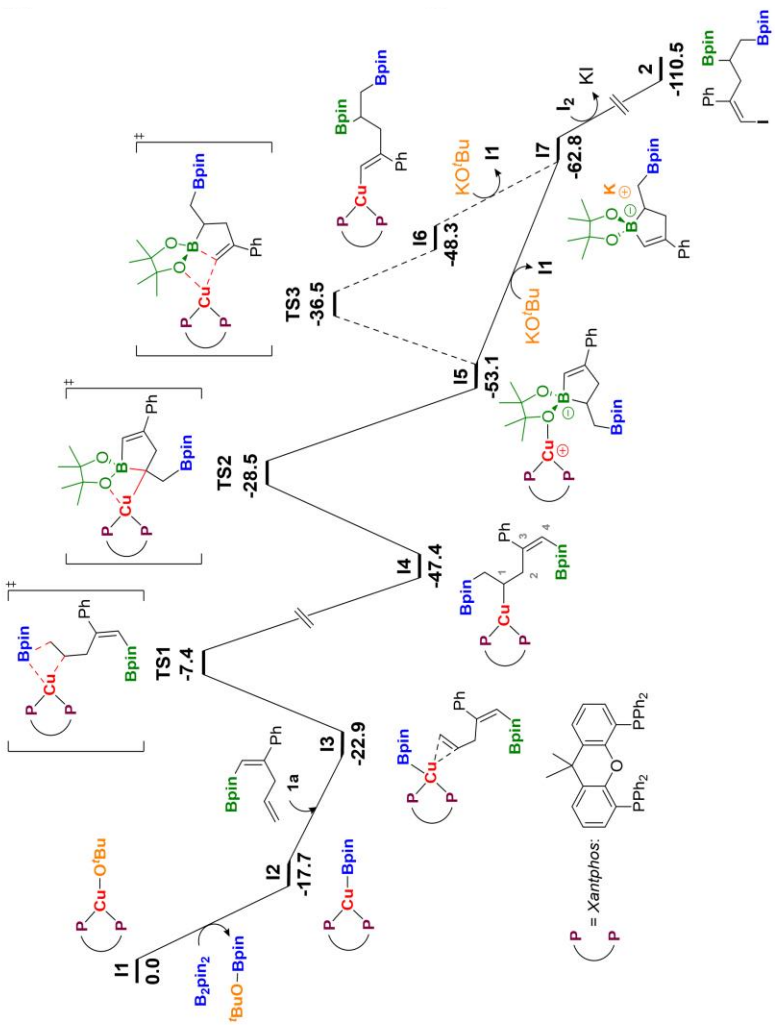


Figure 6.1. Free-energy profile (kcal mol^{-1}) for the borylcupration of skipped (*E*)-diene **6.1a** with B_2pin_2 catalysed by Cu-Xantphos complex in the presence of KO^{t}Bu base, followed by I_2-iodonolysis. DFT calculations carried out by Dr. Solé-Daura and Prof. Carbó.

6.5. Conclusions

In conclusion, we have developed a new methodology for a 1,4-boryl copper shift without the assistance of a heteroatom, promoting a remote 1,4-carbon-to-carbon boryl migration. The use of CuCl/Xantphos facilitated the borylcupration of the borylated skipped (*E*)-dienes, followed by the migration of the Bpin group from C(sp^2) to C(sp^3). This novel remote carbon-to-carbon boryl migration occurred with stereospecificity around the alkene, enabling subsequent stereoselective electrophilic trapping by *in situ* addition of H^+, I_2, or NBS.

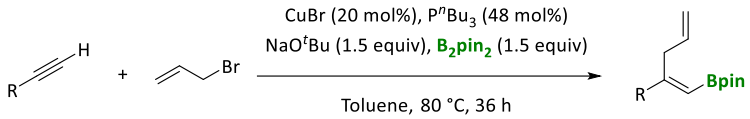
DFT calculations carried out by Dr. Solé-Daura and Prof. Carbó indicated that the 1,4-B/Cu shift proceeds through the nucleophilic attack of the copper-alkyl moiety on the boron atom attached to the C(sp^2) position, forming a 5-membered boracycle intermediate. This boracycle was then trapped electrophilically, completing the 1,4-migration.

Furthermore, we demonstrated the synthetic utility of the novel diborylated (*E*)-iodo substituted alkene by developing a method to prepare functionalised cyclopentenes. This was achieved through a palladium-catalysed regioselective cross-coupling, followed by strategic cyclopropanation using the OH-directed Simmons-Smith reaction, resulting in the stereoselective formation of valuable bicyclic systems.

6.6. Experimental section

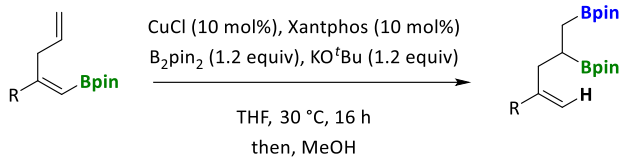
General information. All solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures.[20] Diboron reagents were purchased from Dalian Allychem Co. and were used without further purification. All air-sensitive reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon using Schlenk-type techniques. Flash chromatography purification procedures were performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). Analytical Thin Layer Chromatography (TLC) was performed on Merck Kieselgel 60 F254 and was developed using standard visualising agents: UV fluorescence (254 and 366 nm) or potassium permanganate. NMR spectra were recorded at a Varian 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm ^{1}H and 77.16 ppm ^{13}C). ^{11}B NMR chemical shifts (δ) are reported in ppm relative to $BF_3{\cdot}Et_2O$. Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, sp = septet, m = multiplet. Melting points were measured using open glass capillaries in a Digital Melting Point IA 9100 apparatus. High-Resolution Mass Spectra (HRMS) were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies with an ESI interface that is located at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona), or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or EI interface that is located at the Unidade de Espectrometría de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela).

General procedure for the synthesis of borylated dienes 6.1a-6.1l[8a]



To a mixture of NaO^{t}Bu (290 mg, 3 mmol), CuBr (30 mg, 0.2 mmol), and B_2pin_2 (762 mg, 3 mmol) in toluene (10 ml), were added P^{n}Bu$_3$ (97 mg, 0.48 mmol), phenylacetylene (204 mg, 2 mmol), and allyl bromide (365 mg, 3 mmol) successively. The resultant mixture was stirred at 80 °C for 36 h. The reaction was quenched with ethyl acetate and water, and then extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried with anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 40/1) to give the desired products.

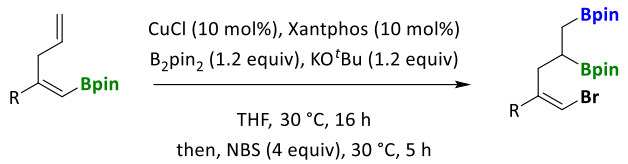
General procedure for Cu-catalysed borylcupration – 1,4-B/Cu shift – protonation



CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added in the vial through the rubber septum. Then, the borylated (*E*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C. After the reaction was complete, the reaction mixture was filtered over Celite. The organic extracts were gently concentrated at the rotary evaporator and the NMR yield was calculated through comparison to an

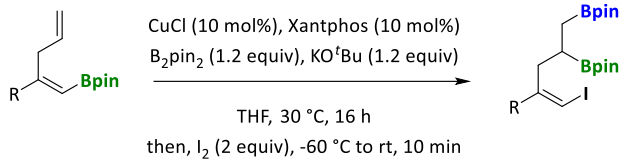
internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to afford the desired product.

General procedure for Cu-catalysed borylcupration – 1,4-B/Cu shift – electrophilic trapping with NBS



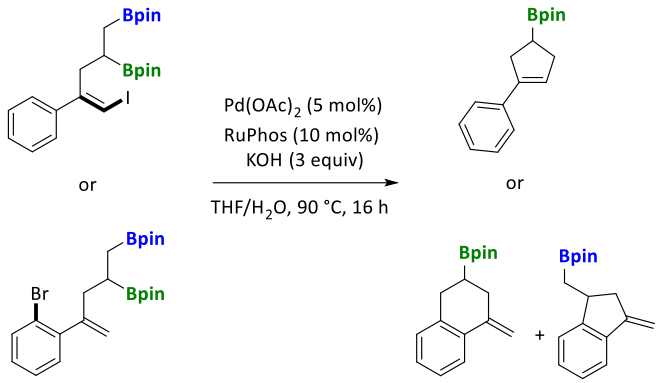
CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1 M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added in the vial through the rubber septum. Then, the borylated (*E*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C and stirred for 16 hours. Subsequently, the NBS (4 equiv, 0.8 mmol) was added, and the temperature was maintained to 30 °C. The mixture was allowed to react for 5 hours at 30 °C until the reaction was completed and then filtered over Celite. The organic extracts were then concentrated under vacuum and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

General procedure for Cu-catalysed borylcupration – 1,4-B/Cu shift – electrophilic trapping with I_2



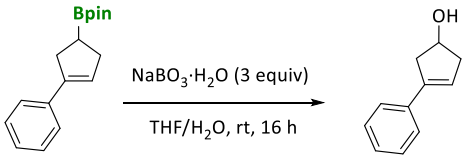
CuCl (0.98 mg, 10 mol%, 0.01 mmol), bis(pinacolato)diboron (60.9 mg, 1.2 equiv, 0.24 mmol) and Xantphos (138.8 mg, 10 mol%, 0.01 mmol) were placed in an oven-dried reaction vial. The vial was sealed with a screw cap containing a Teflon-coated rubber septum. The vial was connected to a vacuum/nitrogen manifold through a needle, evacuated, and backfilled with nitrogen and THF (0.24 ml, 1M). KO^{t}Bu (26.9 mg, 1.2 equiv, 0.24 mmol) in THF (0.24 ml, 1M) was added to the vial through the rubber septum. Then, the borylated (*E*)-skipped dienes (1 equiv, 0.2 mmol) in THF (0.2 ml, 1M) was added dropwise at 30 °C and stirred for 16 hours. Subsequently, iodine (101.5 mg, 2 equiv, 0.4 mmol) was dissolved in 2 mL of THF in a second oven-dried flask. The reaction mixture was then kept at -60 °C while the iodine solution was passed through a Teflon tubing. The cooling bath was removed, and the temperature was allowed to rise to room temperature. After 10 minutes at room temperature, a mixture of 10 mL of saturated aqueous ammonium chloride and 1 mL of saturated sodium bisulfite is added with vigorous stirring. The mixture is filtered through Celite by suction and the contents of the funnel were washed with Et_2O (3 x 15 mL). The inorganic layer is washed twice with pentane. The organic extracts were dried over anhydrous magnesium sulphate and then concentrated under vacuum. The NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

General procedure for intramolecular Suzuki-Miyaura cross-coupling[13]



In a flamed Schlenk-tube equipped with a magnetic stir bar, $Pd(OAc)_2$ (2.25 mg, 5 mol%), RuPhos (9.33, 10 mol%), and the substrate (0.2 mmol) were added in THF (2 mL). Under an argon atmosphere, KOH (33.6 mg, 0.6 mmol, 3 equiv) and deoxygenated water (0.2 mL) were added. The reaction mixture was stirred at 90 °C for 16 h. After that, the mixture was concentrated under vacuum and the NMR yield was calculated through comparison to an internal standard (naphthalene). The crude residue was purified by silica gel flash chromatography to obtain the desired product.

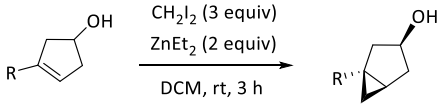
General procedure for the oxidation reaction



In an opened-air flask, charged with a magnetic stir bar, were added the corresponding alkylidenecyclobutanes (0.1 mmol, 1 equiv), $NaBO_3 \cdot H_2O$ (0.3 mmol, 3 equiv), THF (2 mL) and distilled water (1 mL). The reaction was closed with a septum with a needle to avoid over pressures and was stirred for 16 h at room temperature. After this time, the mixture was extracted with Et_2O (3 x 15 mL), the organic layer was dried with anhydrous magnesium sulphate, filtered and the solvents were

evaporated. The crude residue was purified by silica gel chromatography to obtain the corresponding product.

General procedure for Simmons–Smith cyclopropanation reaction[18]

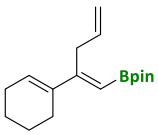


To a solution of the oxidated product (0.2 mmol, 1.0 equiv) in anhydrous DCM (2.0 mL, 0.1 M) was added $ZnEt_2$ (1.0 M in hexane, 0.4 mL, 0.4 mmol, 2.0 equiv) at 0 °C. After stirring for 10 min, CH_2I_2 (161 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was stirred at room temperature and a white precipitate was gradually generated. After 3 hours, the mixture was quenched with saturated aqueous NH_4Cl (8 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered over Celite and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 20/1) to give the corresponding product.

- Characterisation of borylated skipped dienes

Characterisation of compounds **6.1a**-**6.1i** was in agreement with the reported literature.[8a]

(*E*)-2-(2-(Cyclohex-1-en-1-yl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2 dioxaborolane (6.1j)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (40:1). The product was isolated as a colorless oil (50 mg, 90%, >50:1).

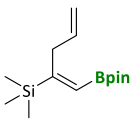
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.12 (bs, 1H), 5.84 (dt, J = 16.7, 10.0 Hz, 1H), 5.39 (s, 1H), 5.06 (dd, J = 17.1, 1.8 Hz, 1H), 4.92 (dd, J = 10.1, 1.6 Hz, 1H), 3.43 (dt, J = 6.5, 1.6 Hz, 2H), 2.17 (bs, 4H), 1.64 (m 2H), 1.55 (m 2H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.2, 138.6, 137.3, 128.0, 114.5, 82.7, 35.8, 26.2, 26.0, 24.8, 23.0, 22.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.1.

HRMS-(ESI+) for **$C_{17}H_{28}BO_2$ [M+H]$^+$:** calculated: 275.2020; found: 275.2019.

(*E*)-Trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-dien-2-yl)silane (6.1k)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (40:1). The product was isolated as a colorless oil (30 mg, 55%, >50:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (s, 1H), 5.77 (dt, J = 16.8, 10.0 Hz, 1H), 5.02 (dd, J = 17.1, 1.8 Hz, 1H), 4.97 – 4.89 (m, 1H), 3.29 (dq, J = 6.7, 1.3 Hz, 2H), 1.26 (s, 12H), 0.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.6, 139.6, 116.0, 84.1, 40.3, 26.1, -0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 28.8.

HRMS-(ESI+) for **$C_{14}H_{28}BO_2Si$ [M+H]$^+$:** calculated: 267.1946; found: 267.1940.

(Z)-4,4,5,5-Tetramethyl-2-(penta-1,4-dien-1-yl)-1,3,2-dioxaborolane (6.1l)

The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (40:1). The product was isolated as a colorless oil (38 mg, 98%, >50:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.42 (m, 1H), 5.83 (dt, *J* = 16.7, 10.1 Hz, 1H), 5.40 (dt, *J* = 13.4, 1.4 Hz, 1H), 5.05 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.98 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.16 (dt, *J* = 6.5, 1.5 Hz, 2H), 1.26 (s, 12H).

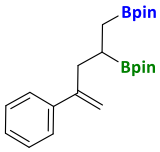
^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.6, 136.9, 115.0, 82.9, 36.6, 24.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 29.6.

HRMS-(ESI+) for **$C_{11}H_{20}BO_2$ [M+H]$^+$:** calculated: 195.1557; found: 195.1559.

- Characterisation of products isolated from Cu-catalysed borylcupration/1,4-B/Cu migration/protonation (or iodination or bromination)

2,2'-(4-Phenylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.2)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (77 mg, 97%).

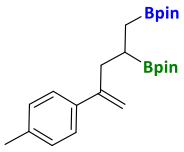
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 – 7.35 (m, 2H), 7.32 – 7.09 (m, 3H), 5.22 (d, J = 1.7 Hz, 1H), 5.04 (d, J = 1.4 Hz, 1H), 2.71 (ddd, J = 14.5, 7.6, 1.2 Hz, 1H), 2.46 (ddd, J = 14.4, 8.1, 1.1 Hz, 1H), 1.19 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.18 (s, 6H), 1.18 (m, 1H), 0.82 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.2, 141.5, 128.0, 127.0, 126.4, 113.0, 82.8, 82.8, 38.8, 24.8, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5.

HRMS-(ESI+) for **$C_{23}H_{37}B_2O_4$ $[M+H]^+$:** calculated: 399.2872; found: 399.2891.

2,2'-(4-(p-Tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.3)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (75 mg, 91%).

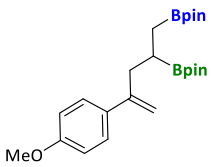
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, J = 8.2 Hz, 2H), 7.13 – 7.06 (m, 2H), 5.22 (d, J = 1.7 Hz, 1H), 5.01 (d, J = 1.5 Hz, 1H), 2.71 (ddd, J = 14.5, 7.6, 1.2 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.32 (s, 3H), 1.22 (s, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 1.21 (s, 6H), 1.21 (m, 1H), 0.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 138.5, 136.7, 128.8, 126.2, 112.2, 82.8, 82.8, 38.8, 24.8, 24.8, 24.8, 24.7, 21.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.3.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 413.3036; found: 413.3038.

2,2'-(4-(4-methoxyphenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.4)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (84 mg, 98%).

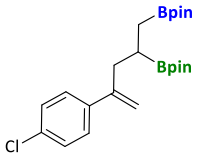
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.32 (m, 2H), 6.86 – 6.77 (m, 2H), 5.18 (d, J = 1.7 Hz, 1H), 4.98 (s, 1H), 3.79 (s, 3H), 2.70 (ddd, J = 14.4, 7.6, 1.2 Hz, 1H), 2.44 (ddd, J = 14.4, 8.1, 1.0 Hz, 1H), 1.21 (m, 1H), 1.21 (s, 6H), 1.21 (s, 6H), 1.20 (s, 12H), 0.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.8, 147.4, 133.9, 127.4, 113.4, 111.5, 82.8, 82.8, 55.2, 38.9, 24.8, 24.8, 24.8, 24.7, 17.0 (C–B), 13.0 (C–B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_5$ [M+H]$^+$:** calculated: 429.2984; found: 429.2978.

2,2'-(4-(4-Chlorophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.5)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (69 mg, 80%).

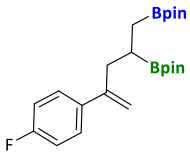
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 – 7.31 (m, 2H), 7.22 – 7.10 (m, 2H), 5.23 (d, J = 1.5 Hz, 1H), 5.07 (d, J = 1.6 Hz, 1H), 2.68 (ddd, J = 14.4, 7.7, 1.2 Hz, 1H), 2.51 – 2.40 (m, 1H), 1.22 (s, 12H), 1.20 (s, 12H), 1.20 (m, 1H), 0.86 – 0.77 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.2, 139.9, 132.8, 128.2, 127.7, 113.5, 82.9, 82.9, 38.7, 24.8, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.3.

HRMS-(ESI+) for **$C_{23}H_{36}B_2ClO_4$ [M+H]$^+$:** calculated: 433.2483; found: 433.2504.

2,2'-(4-(4-Fluorophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.6)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (78 mg, 94%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 – 7.32 (m, 2H), 6.97 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 5.18 (d, J = 1.6 Hz, 1H), 5.04 (d, J = 1.5 Hz, 1H), 2.69 (ddd, J = 14.4, 7.7, 1.2 Hz, 1H), 2.45 (ddd, J = 14.4, 8.0, 1.1 Hz, 1H), 1.21 (s, 12H), 1.20 (s, 12H), 1.20 (m, 1H), 0.83 (m, 2H).

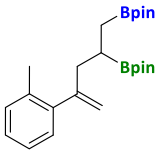
^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz), 147.2, 137.5, 137.4, 127.9 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 113.0, 112.9, 82.9, 82.8, 38.9, 24.8, 24.8, 24.8, 24.7, 16.9(C-B), 11.9(C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -116.05.

HRMS-(ESI+) for **$C_{23}H_{36}B_2FO_4$ [M+H]$^+$:** calculated: 417.2778; found: 417.2787.

2,2'-(4-(o-Tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.7)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (79 mg, 96%).

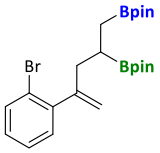
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 – 7.06 (m, 4H), 5.17 (d, J = 1.6 Hz, 1H), 4.85 (d, J = 2.1 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.34 (m, 1H), 2.30 (s, 3H), 1.31 – 1.26 (m, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 0.93 – 0.89 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 143.4, 134.9, 129.9, 128.5, 126.5, 125.2, 114.0, 82.8, 82.8, 41.1, 24.8, 24.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{24}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 413.3036; found: 413.3029.

2,2'-(4-(2-bromophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.8)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (73 mg, 77%).

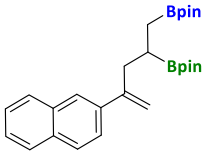
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (dd, J = 8.0, 1.3 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.18 – 7.09 (m, 1H), 5.29 (d, J = 1.6 Hz, 1H), 5.01 (d, J = 1.8 Hz, 1H), 2.74 (ddd, J = 14.8, 8.0, 1.1 Hz, 1H), 2.47 (ddd, J = 14.8, 8.0, 1.1 Hz, 1H), 1.28 (s, 12H), 1.28 (m, 1H), 1.28 (s, 12H), 1.03 – 0.92 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.4, 144.2, 132.5, 130.5, 128.1, 126.9, 122.0, 115.6, 82.9, 82.8, 40.3, 24.8, 24.8, 24.8, 24.7, 16.9(C-B), 11.7(C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{23}H_{36}B_2BrO_4$ [M+H]$^+$:** calculated: 477.1978; found: 477.1973.

2,2'-(4-(Naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.9)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (81 mg, 90%).

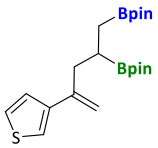
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 – 7.73 (m, 4H), 7.59 (dd, J = 8.6, 1.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 5.39 (d, J = 1.6 Hz, 1H), 5.17 (d, J = 1.4 Hz, 1H), 2.85 (ddd, J = 14.5, 7.7, 1.2 Hz, 1H), 2.60 (ddd, J = 14.4, 8.1, 1.1 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.20 (s, 6H), 1.20 (m, 1H), 0.89 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.1, 138.8, 133.4, 132.7, 128.2, 127.5, 127.4, 125.8, 125.5, 125.1, 124.9, 113.6, 82.9, 82.8, 38.8, 24.8, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.7.

HRMS-(ESI+) for **$C_{27}H_{39}B_2O_4$ [M+H]$^+$:** calculated: 449.3032; found: 449.3029.

2,2'-(4-(Thiophen-3-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.10)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (68 mg, 84%).

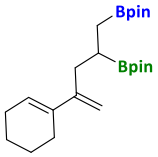
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 – 7.25 (m, 1H), 7.22 (qd, J = 5.0, 2.1 Hz, 2H), 5.33 (d, J = 1.5 Hz, 1H), 5.01 (d, J = 1.3 Hz, 1H), 2.67 (ddd, J = 14.1, 7.7, 1.2 Hz, 1H), 2.40 (ddd, J = 14.2, 7.9, 1.1 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 0.96 – 0.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.6, 142.5, 126.0, 124.9, 120.6, 111.6, 82.9, 39.0, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{23}H_{37}B_2O_4$ [M+H]$^+$:** calculated: 399.2878; found: 399.2889.

2,2'-(4-(Cyclohex-1-en-1-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.11)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (76 mg, 95%).

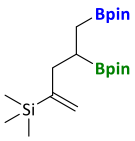
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (m, 1H), 4.92 (d, J = 1.8 Hz, 1H), 4.79 (d, J = 1.7 Hz, 1H), 2.45 (ddd, J = 14.0, 8.0, 1.0 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.13 – 2.07 (m, 4H), 1.70 – 1.58 (m, 2H), 1.54 (m, 2H), 1.38 – 1.28 (m, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 0.85 – 0.77 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.1, 135.5, 124.3, 109.4, 82.8, 82.7, 37.4, 26.0, 25.8, 24.9, 24.8, 24.8, 24.7, 22.9, 22.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{23}H_{41}B_2O_4$ [M+H]$^+$:** calculated: 403.3191; found: 403.3205.

(4,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)trimethylsilane (6.12)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (25 mg, 32%).

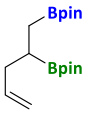
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.56 (dd, J = 3.1, 1.6 Hz, 1H), 5.30 (dd, J = 3.0, 1.1 Hz, 1H), 2.35 (ddd, J = 14.5, 7.8, 1.4 Hz, 1H), 2.08 (ddd, J = 14.6, 8.0, 1.3 Hz, 1H), 1.38 – 1.28 (m, 1H), 1.21 (s, 12H), 1.20 (s, 12H), 0.88 – 0.75 (m, 2H), 0.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 125.6, 84.2, 84.1, 40.9, 32.3, 26.2, 26.2, 26.1, -0.00.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.7.

HRMS-(ESI+) for **$C_{20}H_{41}B_2O_4Si$ [M+H]$^+$:** calculated:395.2798; found: 395.2808.

2,2'-(Pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.13)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (62 mg, 97%).

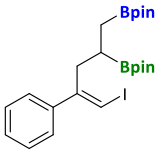
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H), 4.96 (dd, J = 17.1, 2.5 Hz, 1H), 4.90 (dd, J = 10.1, 2.3 Hz, 1H), 2.20 (m, 1H), 2.12 – 2.01 (m, 1H), 1.21 (s, 24H), 1.21 (m, 1H), 0.90 – 0.75 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.7, 114.9, 82.9, 82.8, 37.8, 24.8, 24.8, 24.7, 24.7, 19.5(C-B), 12.9(C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.8.

HRMS-(ESI+) for **$C_{17}H_{33}B_2O_4$ [M+H]$^+$:** calculated: 323.2559; found: 323.2563.

(*E*)-2,2'-(5-Iodo-4-phenylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.14)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (80 mg, 76%).

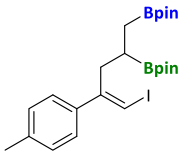
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.20 (m, 5H), 6.34 (s, 1H), 2.86 (dd, J = 13.8, 7.0 Hz, 1H), 2.71 (dd, J = 13.9, 8.6 Hz, 1H), 1.18 (s, 12H), 1.18 (m, 1H), 1.15 (s, 6H), 1.15 (s, 6H), 0.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 141.0, 128.3, 126.8, 113.0, 82.9, 82.8, 79.6, 40.1, 24.9, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.6.

HRMS-(ESI+) for **$C_{23}H_{36}B_2IO_4$ [M+H]$^+$:** calculated: 525.1839; found: 525.1850.

(*E*)-2,2'-(5-Iodo-4-(p-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.15)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (79 mg, 73%).

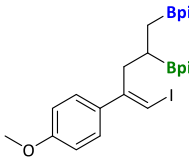
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 – 7.15 (m, 2H), 7.12 – 7.05 (m, 2H), 6.32 (s, 1H), 2.86 (dd, J = 13.8, 6.9 Hz, 1H), 2.71 (dd, J = 13.8, 8.7 Hz, 1H), 2.31 (s, 3H), 1.20 (s, 12H), 1.18 (s, 12H), 1.18 (m, 1H), 0.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 138.1, 137.3, 129.0, 126.7, 82.9, 82.8, 78.8, 40.0, 24.9, 24.9, 24.8, 24.7, 21.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.4.

HRMS-(ESI+) for **$C_{24}H_{38}B_2IO_4$ [M+H]$^+$:** calculated: 539.1995; found: 539.2004.

(*E*)-2,2'-(5-Iodo-4-(4-methoxyphenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.16)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (101 mg, 91%).

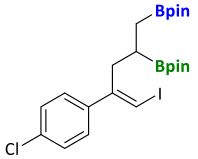
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 6.28 (s, 1H), 3.79 (s, 3H), 2.85 (dd, J = 13.8, 7.0 Hz, 1H), 2.70 (dd, J = 13.8, 8.8 Hz, 1H), 1.20 (s, 6H), 1.20 (s, 6H), 1.18 (s, 12H), 1.18 (m, 1H), 0.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.1, 151.3, 133.5, 127.9, 113.7, 82.9, 82.8, 78.0, 55.2, 40.0, 24.9, 24.9, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.1.

HRMS-(ESI+) for **$C_{24}H_{38}B_2IO_5$ [M+H]$^+$:** calculated: 555.1952; found: 555.1945.

(*E*)-2,2'-(4-(4-Chlorophenyl)-5-iodopent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.17)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (101 mg, 90%).

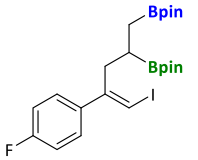
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.15 (m, 4H), 6.34 (s, 1H), 2.81 (dd, J = 13.9, 7.2 Hz, 1H), 2.66 (dd, J = 13.9, 8.6 Hz, 1H), 1.17 (m, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 1.14 (s, 12H), 0.82 – 0.76 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 139.4, 133.4, 128.4, 128.1, 126.9, 83.0, 82.9, 80.1, 40.1, 24.9, 24.9, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.8.

HRMS-(ESI+) for **$C_{23}H_{34}B_2ClIO_4$ [M+H]$^+$:** calculated: 559.1452; found: 559.1449.

(*E*)-2,2'-(4-(4-Fluorophenyl)-5-iodopent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.18)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (95 mg, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (dd, J = 8.9, 5.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 8.8 Hz, 1H), 5.58 (s, 1H), 2.89 – 2.81 (m, 2H), 1.56 – 1.41 (m, 1H), 1.29 (s, 12H), 1.22 (s, 12H), 0.85 – 0.74 (m, 2H).

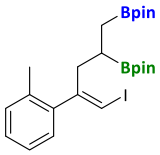
^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.5 (d, $^{1}J_{C\text{-}F}$ = 246.6 Hz), 161.9, 128.0 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 82.8, 82.8, 36.0, 24.8, 24.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.9.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -114.88.

HRMS-(ESI+) for **$C_{23}H_{35}B_2FIO_4$ [M+H]$^+$:** calculated: 543.1745; found: 543.1749.

(*E*)-2,2'-(5-Iodo-4-(o-tolyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.19)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (78 mg, 72%).

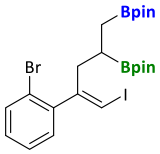
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 – 7.03 (m, 4H), 6.08 (s, 1H), 2.72 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.61 (dd, *J* = 13.7, 8.7 Hz, 1H), 2.25 (s, 3H), 1.20 (m, 1H), 1.20 (s, 6H), 1.20 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 0.96 – 0.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 141.1, 135.1, 130.1, 128.9, 127.2, 125.4, 83.0, 82.8, 80.1, 41.3, 24.9, 24.8, 24.8, 24.7, 19.8, 15.7(C-B), 12.1(C-B).

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.8.

HRMS-(ESI+) for **$C_{24}H_{38}B_2IO_4$ [M+H]$^+$:** calculated: 539.1992; found: 539.1995.

(*E*)-2,2'-(4-(2-Bromophenyl)-5-iodopent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.20)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (105 mg, 87%).

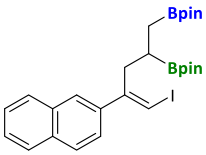
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, J = 8.0 Hz, 1H), 7.40 – 7.22 (m, 2H), 7.20 (d, J = 2.0 Hz, 1H), 6.31 (s, 1H), 2.90 (dd, J = 13.8, 6.3 Hz, 1H), 2.75 (dd, J = 13.9, 9.0 Hz, 1H), 1.27 (s, 24H), 1.04 (m, 1H), 1.04 – 0.93 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 142.0, 132.8, 130.7, 128.7, 127.0, 122.1, 83.0, 82.8, 40.7, 24.9, 24.9, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.5.

HRMS-(ESI+) for **$C_{23}H_{35}B_2BrIO_4$ [M+H]$^+$:** calculated: 603.0944; found: 603.0965.

(*E*)-2,2'-(5-Iodo-4-(naphthalen-2-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.21)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (65 mg, 57%).

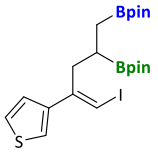
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.73 (m, 4H), 7.50 – 7.39 (m, 3H), 6.51 (s, 1H), 2.99 (dd, J = 13.9, 7.0 Hz, 1H), 2.84 (dd, J = 13.9, 8.7 Hz, 1H), 1.30 – 1.24 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H), 1.15 (s, 6H), 1.14 (s, 6H), 0.89 (d, J = 7.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 138.4, 133.3, 132.8, 128.1, 127.8, 127.5, 126.1, 125.8, 125.8, 125.1, 82.9, 82.8, 80.1, 40.1, 24.9, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{27}H_{38}B_2IO_4$ [M+H]$^+$:** calculated: 575.1995; found: 575.1989.

(*E*)-2,2'-(5-Iodo-4-(thiophen-3-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.22)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (74 mg, 70%).

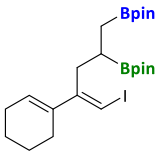
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (m, 1H), 7.23 (m, 1H), 7.12 (dd, J = 5.0, 1.4 Hz, 1H), 6.56 (s, 1H), 2.72 – 2.60 (m, 2H), 1.39 (m, 1H), 1.23 (s, 12H), 1.22 (s, 6H), 1.21 (s, 6H), 0.90 – 0.85 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.0, 141.3, 126.0, 125.3, 121.3, 82.9, 79.0, 40.0, 24.9, 24.9, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.1.

HRMS-(ESI+) for **$C_{21}H_{33}B_2INaO_4S$ [M+Na]$^+$:** calculated: 553.1228; found: 553.1236.

(*E*)-2,2'-(4-(Cyclohex-1-en-1-yl)-5-iodopent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.23)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (91 mg, 86%).

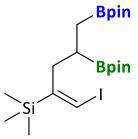
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.17 (s, 1H), 5.83 (m, 1H), 2.58 (dd, J = 13.8, 6.6 Hz, 1H), 2.40 (dd, J = 13.8, 9.1 Hz, 1H), 2.07 (m, 4H), 1.69 – 1.60 (m, 2H), 1.58 – 1.47 (m, 2H), 1.24 (s, 6H), 1.22 (s, 18H), 1.22 (m, 1H), 0.88 – 0.80 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.9, 136.7, 125.9, 82.9, 82.8, 77.5, 37.6, 26.8, 25.7, 24.9, 24.9, 24.8, 24.7, 22.8, 21.9.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.8.

HRMS-(ESI+) for **$C_{23}H_{40}B_2IO_4$ [M+H]$^+$:** calculated: 529.2160; found: 529.2169.

(*E*)-(1-Iodo-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-2-yl)trimethylsilane (6.24)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (54 mg, 52%).

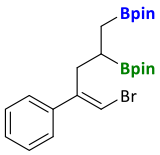
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.55 (s, 1H), 2.51 – 2.42 (m, 1H), 2.27 (ddd, J = 13.4, 10.4, 0.7 Hz, 1H), 1.36 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 0.85 – 0.75 (m, 2H), 0.14 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 93.4, 82.9, 82.8, 42.6, 24.9, 24.9, 24.7, 24.7, -0.5.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.6.

HRMS-(ESI+) for **$C_{20}H_{40}B_2IO_4Si$ [M+H]$^+$:** calculated: 521.1926; found: 521.1928.

(*E*)-2,2'-(5-Bromo-4-phenylpent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.25)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (85 mg, 89%).

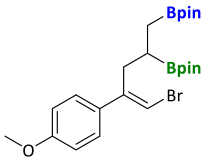
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.18 (m, 5H), 6.28 (s, 1H), 2.78 (m, 2H), 1.18 (s, 6H), 1.17 (m, 1H), 1.17 (s, 6H), 1.15 (s, 6H), 1.14 (s, 6H), 0.82 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 140.3, 128.3, 127.5, 126.9, 105.7, 82.9, 82.8, 35.8, 24.9, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.3.

HRMS-(ESI+) for **$C_{23}H_{36}B_2BrO_4$ [M+H]$^+$:** calculated: 477.1978; found: 477.1972.

(*E*)-2,2'-(5-Bromo-4-(4-methoxyphenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.26)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (85 mg, 84%).

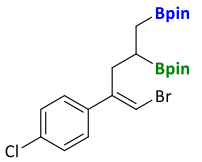
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.17 (s, 1H), 3.73 (s, 3H), 2.71 (m, 2H), 1.14 (m, 1H), 1.14 (s, 6H), 1.13 (s, 6H), 1.11 (s, 6H), 1.11 (s, 6H), 0.75 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 145.7, 132.7, 128.0, 113.8, 104.3, 82.9, 82.8, 55.2, 35.8, 24.9, 24.9, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.1.

HRMS-(ESI+) for **$C_{24}H_{38}B_2BrO_5$ [M+H]$^+$:** calculated: 507.2092; found: 507.2083.

(*E*)-2,2'-(5-Bromo-4-(4-chlorophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.27)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (92 mg, 95%).

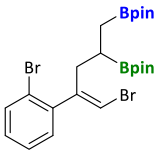
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.24 (m, 4H), 6.35 (s, 1H), 2.91 – 2.73 (m, 2H), 1.25 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.22 (s, 6H), 1.22 (s, 6H), 0.99 – 0.79 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 138.7, 133.4, 128.5, 128.2, 106.6, 83.0, 82.9, 35.8, 24.9, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.3.

HRMS-(ESI+) for **$C_{23}H_{35}B_2BrClO_4$ [M+H]$^+$:** calculated: 511.1596; found: 511.1588.

(*E*)-2,2'-(5-Bromo-4-(2-bromophenyl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.28)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (103 mg, 93%).

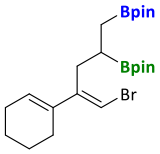
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, J = 7.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.11 (ddd, J = 7.9, 7.0, 2.1 Hz, 1H), 6.16 (s, 1H), 2.76 (m, 2H), 1.20 (s, 24H), 1.16 – 1.06 (m, 1H), 0.97 – 0.89 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 141.3, 132.8, 131.0, 128.9, 127.3, 122.6, 108.1, 83.0, 82.8, 36.6, 24.9, 24.8, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.9.

HRMS-(ESI+) for **$C_{23}H_{35}B_2Br_2O_4$ [M+H]$^+$:** calculated: 555.1083; found: 555.1105.

(*E*)-2,2'-(5-Bromo-4-(cyclohex-1-en-1-yl)pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6.29)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (75 mg, 78%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.16 (s, 1H), 5.85 – 5.80 (m, 1H), 2.55 (dd, J = 13.7, 6.6 Hz, 1H), 2.45 (dd, J = 13.7, 9.2 Hz, 1H), 2.06 (m, 4H), 1.70 – 1.59 (m, 2H), 1.55 (m, 2H), 1.23 (m, 1H), 1.23 (s, 6H), 1.22 (s, 18H), 0.84 (m, 2H).

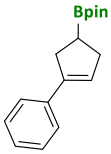
^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 135.7, 125.7, 103.5, 103.5, 82.9, 82.8, 33.1, 26.5, 25.7, 24.6, 24.9, 24.8, 24.7, 22.7, 22.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.3.

HRMS-(ESI+) for **$C_{23}H_{39}B_2BrNaO_4$ [M+Na]$^+$:** calculated: 503.2115; found: 503.2110.

- Characterisation of cross-coupling products and corresponding alcohols after oxidation

4,4,5,5-Tetramethyl-2-(3-phenylcyclopent-3-en-1-yl)-1,3,2-dioxaborolane (6.30)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (45 mg, 84%).

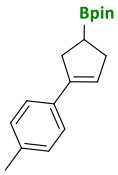
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 – 7.40 (m, 2H), 7.30 (dd, J = 7.8, 6.9 Hz, 2H), 7.23 – 7.16 (m, 1H), 6.17 (m, 1H), 2.89 (m, 1H), 2.83 – 2.65 (m, 2H), 2.58 (m, 1H), 1.83 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.4, 136.7, 128.2, 126.7, 126.1, 125.6, 83.1, 35.7, 35.6, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.4.

HRMS-(ESI+) for **$C_{17}H_{24}BO_2$ [M+H]$^+$:** calculated: 271.1864; found: 271.1860.

4,4,5,5-Tetramethyl-2-(3-(p-tolyl)cyclopent-3-en-1-yl)-1,3,2-dioxaborolane (6.31)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (37 mg, 65%).

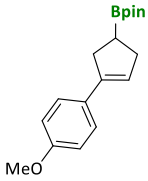
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.30 (m, 2H), 7.14 – 7.07 (m, 2H), 6.10 (m, 1H), 2.87 (m, 1H), 2.81 – 2.63 (m, 2H), 2.57 (m, 1H), 2.33 (s, 3H), 1.82 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 136.4, 133.9, 128.9, 125.5, 125.0, 83.1, 35.6, 24.8, 24.7, 21.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.5.

HRMS-(ESI+) for **$C_{18}H_{26}BO_2$ [M+H]$^+$:** calculated: 285.2026; found: 285.2018.

2-(3-(4-Methoxyphenyl)cyclopent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.32)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (52 mg, 87%).

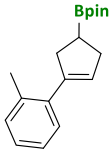
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, J = 8.8 Hz, 2H), 6.88 – 6.80 (m, 2H), 6.02 (m, 1H), 3.80 (s, 3H), 2.92 – 2.81 (m, 1H), 2.77 – 2.62 (m, 2H), 2.62 – 2.49 (m, 1H), 1.89 – 1.75 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.5, 141.7, 129.6, 126.7, 123.9, 113.6, 83.1, 55.2, 35.7, 35.6, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.5.

HRMS-(ESI+) for **$C_{18}H_{26}BO_3$ [M+H]$^+$:** calculated: 301.1965; found: 301.1970.

4,4,5,5-Tetramethyl-2-(3-(o-tolyl)cyclopent-3-en-1-yl)-1,3,2-dioxaborolane (6.33)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (53 mg, 93%).

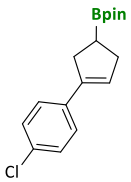
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 – 7.05 (m, 4H), 5.75 (m, 1H), 2.84 – 2.73 (m, 2H), 2.77 – 2.63 (m, 1H), 2.58 (m, 1H), 2.36 (s, 3H), 1.87 – 1.74 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 138.1, 135.5, 130.3, 129.3, 128.0, 126.4, 125.4, 83.1, 38.9, 35.9, 24.7, 21.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.7.

HRMS-(ESI+) for **$C_{18}H_{26}BO_2$ [M+H]$^+$:** calculated: 285.2026; found: 285.2031.

2-(3-(4-Chlorophenyl)cyclopent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.34)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (52 mg, 85%).

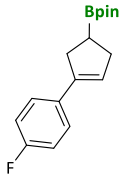
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 8.5 Hz, 2H), 7.30 – 7.20 (m, 2H), 6.18 – 6.12 (m, 1H), 2.84 (m, 1H), 2.78 – 2.63 (m, 2H), 2.57 (m, 1H), 1.89 – 1.75 (m, 1H), 1.26 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.3, 135.2, 132.3, 128.3, 126.8, 126.8, 83.2, 35.7, 35.6, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.5.

HRMS-(ESI+) for **$C_{17}H_{23}BClO_2$ [M+H]$^+$:** calculated: 305.1480; found: 305.1489.

2-(3-(4-Fluorophenyl)cyclopent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.35)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (55 mg, 96%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.34 (m, 2H), 7.03 – 6.90 (m, 2H), 6.12 – 6.06 (m, 1H), 2.90 – 2.79 (m, 1H), 2.79 – 2.64 (m, 2H), 2.57 (m, 1H), 1.90 – 1.76 (m, 1H), 1.27 (s, 12H).

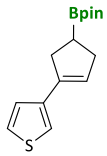
^{13}C NMR ($CDCl_3$, 100 MHz) δ161.8 (d, $^{1}J_{C-F}$ = 245.6 Hz), 141.3, 132.9, 132.9, 127.1 (d, $^{3}J_{C-F}$ = 7.9 Hz), 125.7, 125.7, 115.0 (d, $^{2}J_{C-F}$ = 21.4 Hz), 83.2, 35.8, 35.7, 24.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.3.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -115.86.

HRMS-(ESI+) for **$C_{17}H_{23}BFO_2$ [M+H]$^+$:** calculated: 289.1775; found: 289.1778.

4,4,5,5-Tetramethyl-2-(3-(thiophen-3-yl)cyclopent-3-en-1-yl)-1,3,2-dioxaborolane (6.36)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (44 mg, 79%).

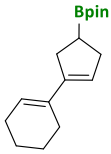
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 2.1 Hz, 2H), 7.07 (t, J = 2.1 Hz, 1H), 6.03 – 5.97 (m, 1H), 2.91 – 2.80 (m, 1H), 2.80 – 2.62 (m, 2H), 2.62 – 2.49 (m, 1H), 1.88 – 1.74 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.9, 137.9, 125.8, 125.5, 125.3, 119.8, 83.1, 36.1, 35.5, 24.8, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.7.

HRMS-(ESI+) for **$C_{15}H_{22}BO_2S$ [M+H]$^+$:** calculated: 277.1422; found: 277.1434.

2-(3-(Cyclohex-1-en-1-yl)cyclopent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.37)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (49 mg, 90%).

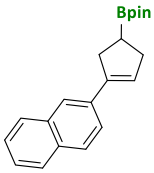
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.70 (m, 1H), 5.64 – 5.60 (m, 1H), 2.72 – 2.61 (m, 1H), 2.60 – 2.40 (m, 4H), 2.21 (m, 2H), 2.13 (m, 2H), 1.70 – 1.63 (m, 2H), 1.60 – 1.52 (m, 2H), 1.25 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 133.5, 124.5, 123.5, 83.0, 35.3, 34.5, 26.2, 25.7, 24.7, 22.8, 22.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.0.

HRMS-(ESI+) for **$C_{17}H_{28}BO_2$ [M+H]$^+$:** calculated: 275.2177; found: 275.2175.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)cyclopent-3-en-1-yl)-1,3,2-dioxaborolane (6.38)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (60 mg, 94%).

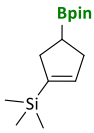
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 – 7.66 (m, 5H), 7.50 – 7.37 (m, 2H), 6.35 – 6.29 (m, 1H), 3.03 (m, 1H), 2.91 (m, 1H), 2.77 (m, 1H), 2.64 (m, 1H), 1.96 – 1.85 (m, 1H), 1.29 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.4, 134.0, 133.6, 132.5, 128.0, 127.6, 127.5, 126.9, 126.0, 125.4, 124.3, 124.1, 83.2, 35.8, 35.6, 24.8, 24.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.7.

HRMS-(ESI+) for **$C_{21}H_{26}BO_2$ [M+H]$^+$:** calculated: 321.2020; found: 321.2031.

Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-en-1-yl)silane (6.39)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (52 mg, 97%).

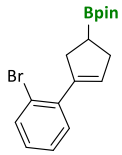
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.99 – 5.92 (m, 1H), 2.65 – 2.49 (m, 2H), 2.40 – 2.25 (m, 2H), 1.60 – 1.52 (m, 1H), 1.25 (s, 12H), 0.06 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 141.9, 84.6, 40.0, 39.0, 26.3, -0.00.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.6.

HRMS-(ESI+) for **$C_{14}H_{28}BO_2Si$ [M+H]$^+$:** calculated: 267.1952; found: 267.1964.

2-(3-(2-Bromophenyl)cyclopent-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.50)



The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (61 mg, 88%).

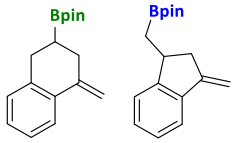
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, J = 8.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.06 (dd, J = 8.0, 5.3 Hz, 1H), 5.97 (m, 1H), 2.89 (m, 1H), 2.84 – 2.74 (m, 1H), 2.69 (m, 1H), 2.57 (m, 1H), 1.91 – 1.76 (m, 1H), 1.27 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.8, 139.5, 133.1, 131.2, 129.9, 127.9, 126.9, 125.6, 122.2, 83.1, 38.4, 35.7, 24.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.9.

HRMS-(ESI+) for **$C_{17}H_{23}BBrO_2$ [M+H]$^+$:** calculated: 349.0963; found 349.0967.

4,4,5,5-Tetramethyl-2-(4-methylene-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-((3-methylene-2,3-dihydro-1H-inden-1-yl)methyl)-1,3,2-dioxaborolane (6.52-6.53)



The products were purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The products were isolated as a mixture of a colorless oil (20 mg, 36%, 1:1 ratio).

Product 6.52: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 – 7.60 (m, 1H), 7.48 – 7.43 (m, 1H), 7.25 – 7.16 (m, 2H), 5.41 (t, J = 2.5 Hz, 1H), 5.01 (t, J = 2.1 Hz, 1H), 3.39 (tt, J = 9.9, 5.3 Hz, 1H), 2.51 – 2.35 (m, 2H), 1.35 (dd, J = 15.6, 5.0 Hz, 1H), 1.26 (s, 6H), 1.26 (s, 6H), 1.01 (dd, J = 15.6, 9.7 Hz, 1H).

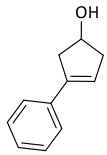
Product 6.53: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.27 (m, 1H), 7.18 – 7.08 (m, 3H), 5.45 (m, 1H), 4.95 (m, 1H), 3.06 (ddt, J = 16.3, 8.1, 2.1 Hz, 1H), 2.95 – 2.77 (m, 2H), 2.73 – 2.65 (m, 1H), 1.53 – 1.43 (m, 1H), 1.25 (s, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.7, 150.2, 149.4, 145.1, 143.5, 140.4, 137.7, 137.6, 136.1, 134.6, 128.9, 128.3, 127.4, 126.4, 126.1, 125.7, 124.6, 124.2, 124.2, 122.6, 120.3, 118.7, 107.5, 102.3, 83.2, 83.1, 44.6, 40.9, 38.1, 34.3, 31.7, 24.9, 24.9, 24.7, 24.7, 24.7, 12.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.1.

HRMS-(ESI+) for **$C_{17}H_{24}BO_2$ [M+H]$^+$**: calculated: 271.1864; found: 271.1869.

3-Phenylcyclopent-3-en-1-ol (6.40)



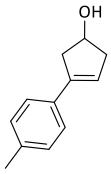
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (29 mg, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 – 7.33 (m, 2H), 7.32 – 7.21 (m, 2H), 7.20 – 7.08 (m, 2H), 6.05 (dt, *J* = 3.9, 2.0 Hz, 1H), 4.57 (tt, *J* = 6.3, 2.4 Hz, 1H), 2.96 (ddq, *J* = 16.5, 6.1,

1.9 Hz, 1H), 2.81 (ddq, *J* = 17.9, 6.1, 1.9 Hz, 1H), 2.63 (ddq, *J* = 16.5, 2.8, 1.4 Hz, 1H), 2.44 (dtt, *J* = 17.9, 2.8, 1.5 Hz, 1H), 1.83 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 136.1, 128.3, 127.2, 125.6, 122.9, 71.8, 43.4, 43.3.

3-(p-Tolyl)cyclopent-3-en-1-ol (6.41)

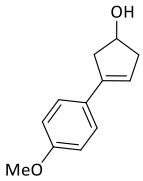


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (28 mg, 80%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.30 (m, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.07 (bs, 1H), 4.65 (m, 1H), 3.03 (dd, J = 16.5, 6.1 Hz, 1H), 2.88 (dd, J = 17.9, 6.2 Hz, 1H), 2.69 (dd, J = 16.5, 2.6 Hz, 1H), 2.51 (dd, J = 17.8, 2.3 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9, 137.0, 133.3, 129.0, 125.5, 121.8, 71.9, 43.4, 43.4, 21.1.

3-(4-Methoxyphenyl)cyclopent-3-en-1-ol (6.42)

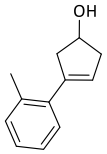


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (31 mg, 81%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.34 (m, 2H), 6.89 – 6.82 (m, 2H), 5.99 (bs, 1H), 4.64 (m, 1H), 3.81 (s, 3H), 3.07 – 2.95 (m, 1H), 2.88 (dd, J = 17.6, 6.1 Hz, 1H), 2.68 (dd, J = 16.4, 2.6 Hz, 1H), 2.55 – 2.46 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 39.4, 129.0, 126.7, 120.6, 113.7, 71.9, 55.2, 43.4, 43.4.

3-(o-Tolyl)cyclopent-3-en-1-ol (6.43)

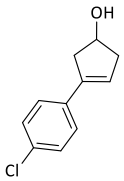


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (34 mg, 97%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 – 7.10 (m, 4H), 5.74 (bs, 1H), 4.63 (m, 1H), 3.03 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.89 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.66 (dd, *J* = 16.6, 2.9 Hz, 1H), 2.53 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.9, 137.3, 135.6, 130.5, 128.1, 126.9, 126.2, 125.6, 125.5, 71.9, 46.5, 43.5, 21.2.

3-(4-Chlorophenyl)cyclopent-3-en-1-ol (6.44)

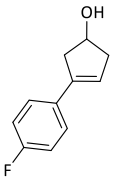


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (37 mg, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, J = 8.6 Hz, 2H), 7.24 – 7.12 (m, 2H), 6.05 (bs, 1H), 4.59 (m, 1H), 2.94 (dd, J = 16.5, 6.1 Hz, 1H), 2.82 (dd, J = 18.0, 6.2 Hz, 1H), 2.60 (dd, J = 16.5, 2.9 Hz, 1H), 2.45 (dd, J = 18.0, 2.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.0, 134.6, 132.8, 128.5, 126.8, 123.6, 71.7, 43.5, 43.3.

3-(4-Fluorophenyl)cyclopent-3-en-1-ol (6.45)



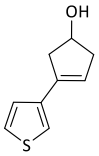
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (32 mg, 90%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 – 7.34 (m, 2H), 7.05 – 6.95 (m, 2H), 6.04 (bs, 1H), 4.65 (m, 1H), 3.00 (dd, J = 16.4, 6.1 Hz, 1H), 2.93 – 2.83 (m, 1H), 2.67 (ddd, J = 16.4, 2.7 Hz, 1H), 2.60 – 2.46 (m, 1H), 1.83 (bs, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.0 (d, $^{1}J_{C-F}$ = 246.5 Hz), 138.9, 132.3, 132.3, 127.1 (d, $^{3}J_{C-F}$ = 7.9 Hz), 122.5, 115.2 (d, $^{2}J_{C-F}$ = 21.4 Hz), 71.7, 43.4, 43.4.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -114.99.

3-(Thiophen-3-yl)cyclopent-3-en-1-ol (6.46)

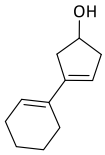


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (25 mg, 74%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (dd, J = 5.0, 2.7 Hz, 1H), 7.25 (d, J = 1.5 Hz, 1H), 7.10 (dt, J = 2.1, 1.0 Hz, 1H), 5.95 (bs, 1H), 4.66 – 4.61 (m, 1H), 3.01 (dd, J = 16.4, 6.3 Hz, 1H), 2.95 – 2.81 (m, 1H), 2.67 (dd, J = 16.4, 2.7 Hz, 1H), 2.50 (dd, J = 17.9, 2.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.4, 135.5, 125.7, 125.5, 122.2, 120.4, 71.8, 43.8, 43.3.

3-(Cyclohex-1-en-1-yl)cyclopent-3-en-1-ol (6.47)

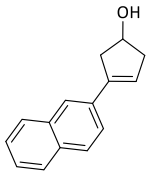


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (29 mg, 89%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.74 – 5.69 (m, 1H), 5.59 – 5.55 (m, 1H), 4.53 (tt, J = 6.2, 2.3 Hz, 1H), 2.76 (ddt, J = 17.4, 6.4, 2.3 Hz, 2H), 2.43 (m, 2H), 2.29 – 2.18 (m, 2H), 2.16 – 2.11 (m, 2H), 1.67 (q, J = 6.4, 6.0 Hz, 2H), 1.63 – 1.50 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 133.4, 125.3, 120.2, 71.7, 43.1, 42.3, 29.7, 25.8, 25.7, 22.7, 22.3.

3-(Naphthalen-2-yl)cyclopent-3-en-1-ol (6.48)

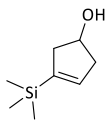


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (39 mg, 92%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 – 7.64 (m, 5H), 7.50 – 7.39 (m, 2H), 6.27 (dt, J = 3.9, 1.9 Hz, 1H), 4.72 (bs, 1H), 3.22 – 3.11 (m, 1H), 2.96 (dd, J = 18.0, 6.2 Hz, 1H), 2.85 (dd, J = 16.4, 2.7 Hz, 1H), 2.59 (dd, J = 18.0, 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.1, 133.5, 132.7, 128.0, 127.8, 127.6, 126.2, 125.7, 124.3, 123.9, 123.7, 71.9, 43.6, 43.3.

3-(trimethylsilyl)cyclopent-3-en-1-ol (6.49)

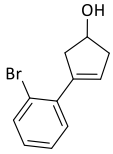


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (28 mg, 90%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94 (bs, 1H), 4.53 (m, 1H), 2.75 – 2.60 (m, 2H), 2.46 – 2.29 (m, 2H), 0.09 (s, 9H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 135.9, 72.2, 45.9, 38.7, 0.0

3-(2-Bromophenyl)cyclopent-3-en-1-ol (6.51)



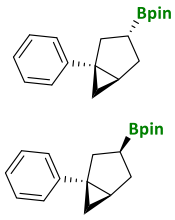
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (46 mg, 96%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (dd, J = 8.0, 1.1 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.11 (m, 1H), 5.91 (bs, 1H), 4.63 (m, 1H), 3.15 – 3.03 (m, 1H), 2.87 (dd, J = 17.5, 5.8 Hz, 1H), 2.75 (dd, J = 16.6, 2.7 Hz, 1H), 2.53 (dd, J = 17.5, 2.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.8, 133.1, 130.1, 128.4, 128.1, 127.1, 125.6, 122.2, 72.3, 46.0, 43.3.

- Characterisation of bicycles

4,4,5,5-Tetramethyl-2-((1S,3R,5S)-1-phenylbicyclo[3.1.0]hexan-3-yl)-1,3,2-dioxaborolane and 4,4,5,5-tetramethyl-2-((1S,3S,5S)-1-phenylbicyclo[3.1.0]hexan-3-yl)-1,3,2-dioxaborolane (6.54)



The products were purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The products were isolated as a colorless oil (52 mg, 92%).

Product 6.54a: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.27 – 7.23 (m, 2H), 7.18 (ddd, J = 8.3, 3.4, 1.5 Hz, 2H), 7.16 – 7.09 (m, 1H), 2.35 – 2.25 (m, 1H), 2.22 – 2.13 (m, 1H), 2.09 – 1.99 (m, 1H), 1.69 – 1.58 (m, 2H), 1.24 (s, 12H), 0.97 – 0.92 (m, 1H), 0.75 – 0.70 (m, 1H).

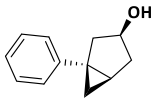
Product 6.54b: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 – 7.23 (m, 2H), 7.18 (ddd, J = 8.3, 3.4, 1.5 Hz, 2H), 7.16 – 7.09 (m, 1H), 2.35 – 2.25 (m, 1H), 2.22 – 2.13 (m, 1H), 2.09 – 1.99 (m, 1H), 1.69 – 1.58 (m, 2H), 1.26 (s, 12H), 0.97 – 0.92 (m, 1H), 0.75 – 0.70 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 145.6, 129.4, 128.7, 128.1, 128.0, 128.0, 127.4, 126.1, 125.6, 125.0, 83.2, 83.0, 34.3, 34.0, 32.6, 32.5, 30.2, 29.8, 27.2, 27.1, 24.8, 24.7, 18.4, 16.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 35.0.

HRMS-(ESI+) for $C_{18}H_{26}BO_2$ $[M+H]^+$: calculated: 285.2026; found: 285.2031.

1-Phenylbicyclo[3.1.0]hexan-3-ol (6.55-*syn*)

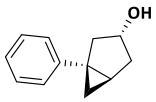


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (18 mg, 52% from **6.54**) (33 mg, 95% from **6.41**).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.32 (m, 2H), 7.30 – 7.20 (m, 3H), 4.61 (m, 1H), 2.52 (dd, J = 13.9, 6.5 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.27 (d, J = 14.0 Hz, 1H), 1.98 (d, J = 14.2 Hz, 1H), 1.80 (dt, J = 8.9, 4.7 Hz, 1H), 1.72 – 1.66 (m, 1H), 1.48 (t, J = 4.5 Hz, 1H), 1.10 – 1.01 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 128.2, 126.0, 125.3, 73.2, 42.7, 38.7, 32.6, 26.8, 21.9.

1-Phenylbicyclo[3.1.0]hexan-3-ol (6.55-*anti*)

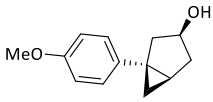


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (9 mg, 26%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 – 7.25 (m, 2H), 7.16 (m, 3H), 4.16 (m, 1H), 2.58 (dd, J = 12.3, 7.0 Hz, 1H), 2.31 (dd, J = 12.4, 7.1 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.94 – 1.81 (m, 1H), 1.66 (dt, J = 8.3, 4.7 Hz, 1H), 1.42 (d, J = 12.9 Hz, 1H), 1.32 – 1.20 (m, 1H), 0.82 – 0.74 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.7, 128.2, 125.7, 125.4, 71.1, 41.2, 37.1, 29.7, 24.8, 19.2.

1-(4-Methoxyphenyl)bicyclo[3.1.0]hexan-3-ol (6.56)

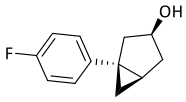


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (40 mg, 98%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 – 7.07 (m, 2H), 6.87 – 6.79 (m, 2H), 4.55 – 4.48 (m, 1H), 3.79 (s, 3H), 2.43 – 2.26 (m, 2H), 2.15 (d, J = 14.0 Hz, 1H), 1.87 (d, J = 14.1 Hz, 1H), 1.67 – 1.56 (m, 1H), 1.49 (s, 1H), 1.31 (t, J = 4.4 Hz, 1H), 0.91 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.5, 137.3, 127.4, 113.7, 73.4, 55.3, 43.5, 38.8, 32.2, 26.2, 21.0.

1-(4-Fluorophenyl)bicyclo[3.1.0]hexan-3-ol (6.57)



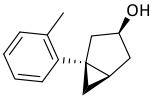
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (34 mg, 89%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 – 7.07 (m, 2H), 7.00 – 6.90 (m, 2H), 4.52 (m, 1H), 2.42 – 2.28 (m, 2H), 2.16 (d, J = 13.9 Hz, 1H), 1.88 (d, J = 14.2 Hz, 1H), 1.72 – 1.61 (m, 1H), 1.51 (s, 2H), 1.36 (t, J = 4.5 Hz, 1H), 0.91 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ160.9 (d, *J* = 243.3 Hz), 140.9, 140.8, 127.7 (d, *J* = 7.8 Hz), 114.9 (d, *J* = 21.1 Hz), 73.2, 43.2, 38.7, 32.2, 26.5, 21.4.

^{19}F NMR ($CDCl_3$, 377 MHz) δ -117.34.

1-(o-Tolyl)bicyclo[3.1.0]hexan-3-ol (6.58)

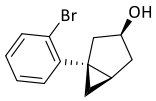


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (33 mg, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 – 7.22 (m, 1H), 7.17 – 7.07 (m, 3H), 4.53 (m, 1H), 2.46 (m, 1H), 2.40 (s, 3H), 2.23 – 2.06 (m, 2H), 1.93 (d, J = 14.3 Hz, 1H), 1.60 (d, J = 8.8 Hz, 1H), 1.28 (d, J = 8.2 Hz, 1H), 0.87 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.4, 138.2, 130.1, 129.4, 126.4, 125.7, 73.8, 44.5, 39.0, 33.3, 24.9, 19.5, 18.7.

1-(2-Bromophenyl)bicyclo[3.1.0]hexan-3-ol (6.59)

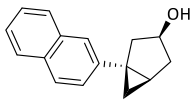


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (42 mg, 83%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 4.51 – 4.43 (m, 1H), 2.47 (m, 1H), 2.29 (m, 1H), 1.99 (d, J = 14.1 Hz, 1H), 1.85 (d, J = 14.1 Hz, 1H), 1.54 (dd, J = 8.8, 4.5 Hz, 1H), 1.27 (m, 1H), 0.92 – 0.82 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 132.8, 132.2, 128.2, 128.0, 127.2, 126.0, 73.7, 43.9, 39.0, 35.2, 25.9, 18.6.

1-(Naphthalen-2-yl)bicyclo[3.1.0]hexan-3-ol (6.60)

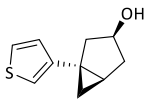


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (43 mg, 96%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 – 7.72 (m, 3H), 7.64 (d, J = 1.9 Hz, 1H), 7.43 (m, 2H), 7.29 – 7.22 (m, 1H), 4.62 – 4.54 (m, 1H), 2.55 (dd, J = 14.0, 6.6 Hz, 1H), 2.39 (dd, J = 14.2, 6.2 Hz, 1H), 2.29 (d, J = 14.0 Hz, 1H), 1.95 (d, J = 14.2 Hz, 1H), 1.83 (m, 1H), 1.47 (t, J = 4.6 Hz, 1H), 1.09 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.6, 133.4, 131.7, 127.8, 127.5, 127.3, 126.0, 125.0, 124.9, 124.3, 73.3, 42.9, 38.7, 33.0, 26.9, 21.7.

1-(Thiophen-3-yl)bicyclo[3.1.0]hexan-3-ol (6.61)

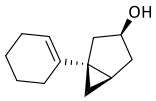


The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (33 mg, 92%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 – 7.22 (m, 1H), 6.90 (dd, J = 3.0, 1.4 Hz, 1H), 6.80 (dd, J = 5.1, 1.4 Hz, 1H), 4.55 – 4.48 (m, 1H), 2.46 (dd, J = 14.0, 6.5 Hz, 1H), 2.37 – 2.25 (m, 1H), 2.14 (d, J = 14.0 Hz, 1H), 1.85 (d, J = 13.9 Hz, 1H), 1.62 (m, 1H), 1.37 (t, J = 4.6 Hz, 1H), 1.00 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.1, 125.8, 124.7, 118.1, 73.2, 41.9, 38.6, 31.5, 27.7, 21.4.

1-(Cyclohex-1-en-1-yl)bicyclo[3.1.0]hexan-3-ol (6.62)



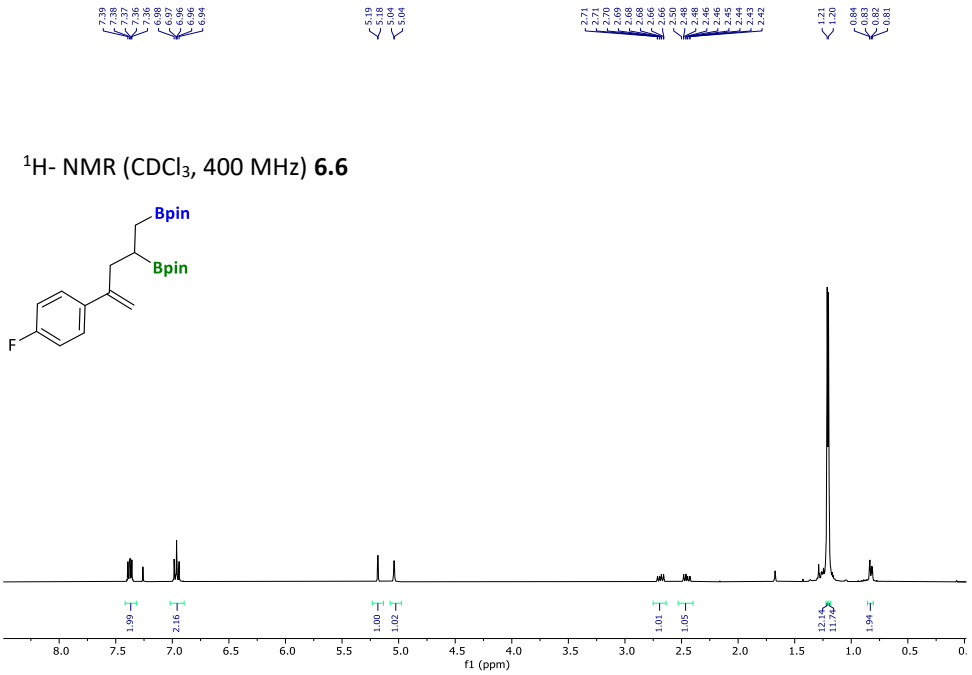
The product was purified by flash chromatography using as eluent a mixture of petroleum ether/diethyl ether (100:5). The product was isolated as a colorless oil (32 mg, 90%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.47 (bs, 1H), 4.40 (t, J = 6.6 Hz, 1H), 2.24 – 2.14 (m, 2H), 2.00 (bs, 2H), 1.85 – 1.72 (m, 4H), 1.57 (m, 4H), 1.37 (m, 1H), 0.93 (t, J = 4.4 Hz, 1H), 0.80 – 0.71 (m, 1H).

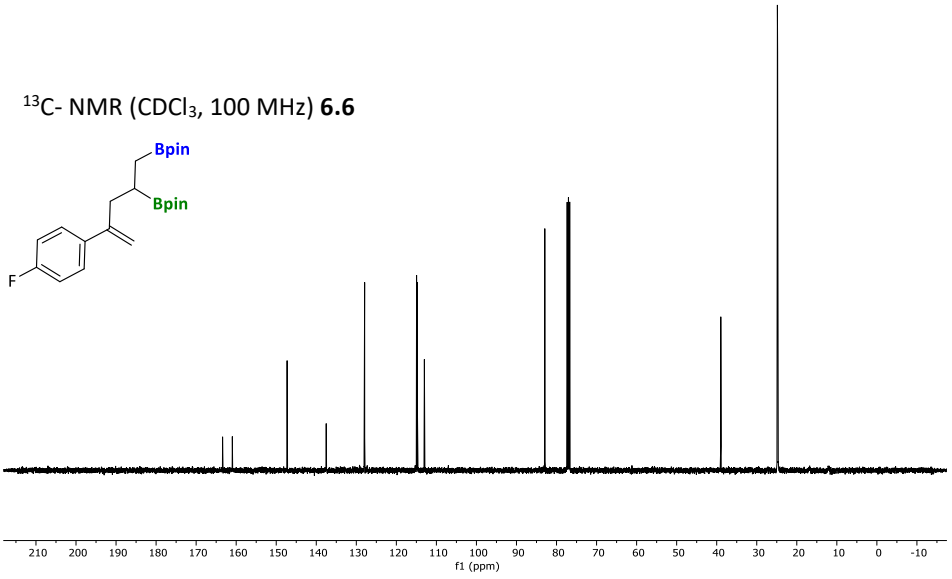
^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 120.0, 73.2, 41.6, 38.5, 34.6, 26.1, 25.3, 23.5, 23.0, 22.6, 17.3.

- Selected NMR spectra

^{1}H- NMR ($CDCl_3$, 400 MHz) **6.6**

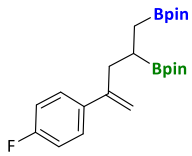


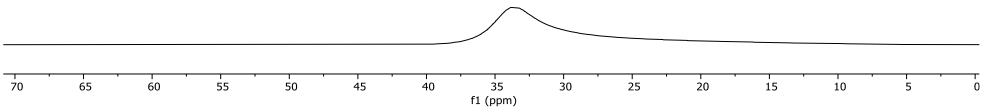
^{13}C- NMR ($CDCl_3$, 100 MHz) **6.6**



— 33.56

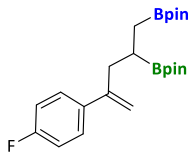
^{11}B NMR ($CDCl_3$, 128.3 MHz) **6.6**

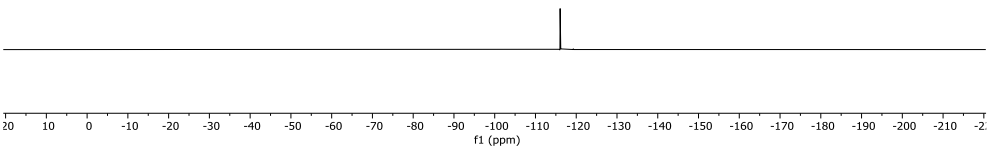




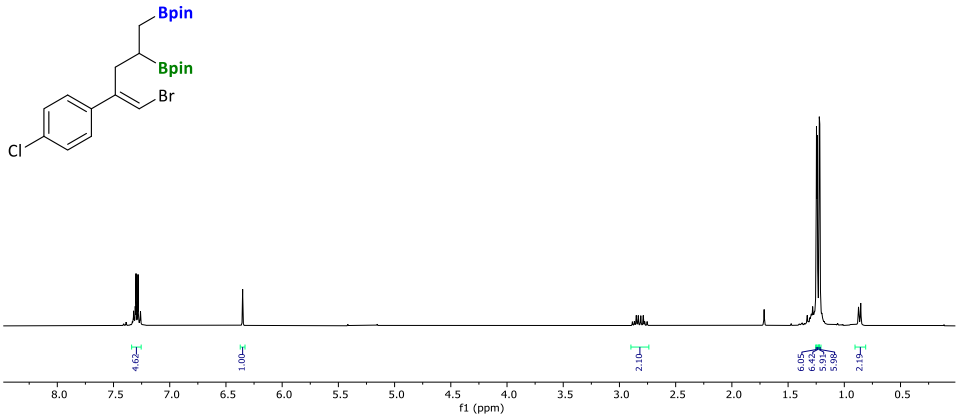
— -116.05

^{19}F NMR ($CDCl_3$, 377 MHz) **6.6**

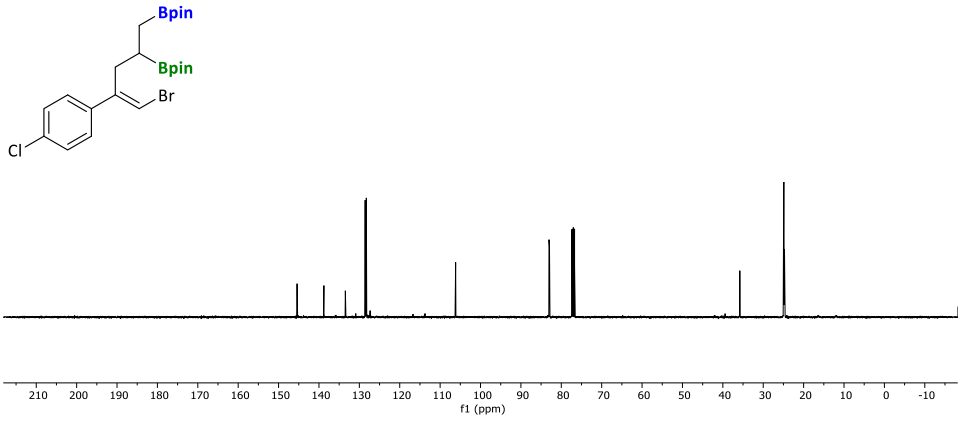




^{1}H- NMR ($CDCl_3$, 400 MHz) **6.27**

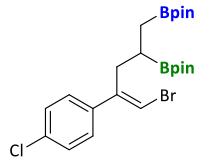


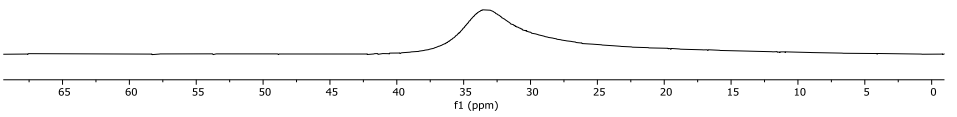
^{13}C- NMR ($CDCl_3$, 100 MHz) **6.27**



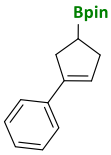
33.31

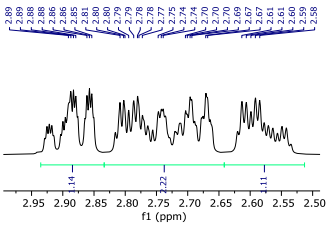
^{11}B NMR ($CDCl_3$, 128.3 MHz) **6.27**

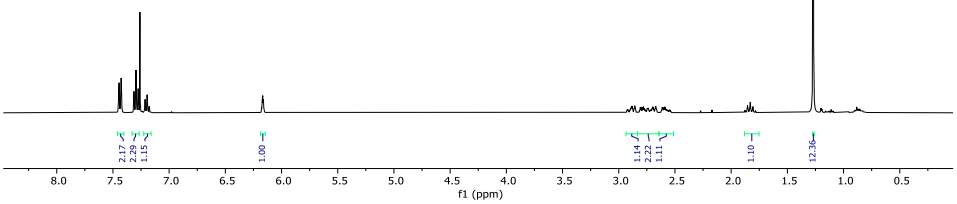




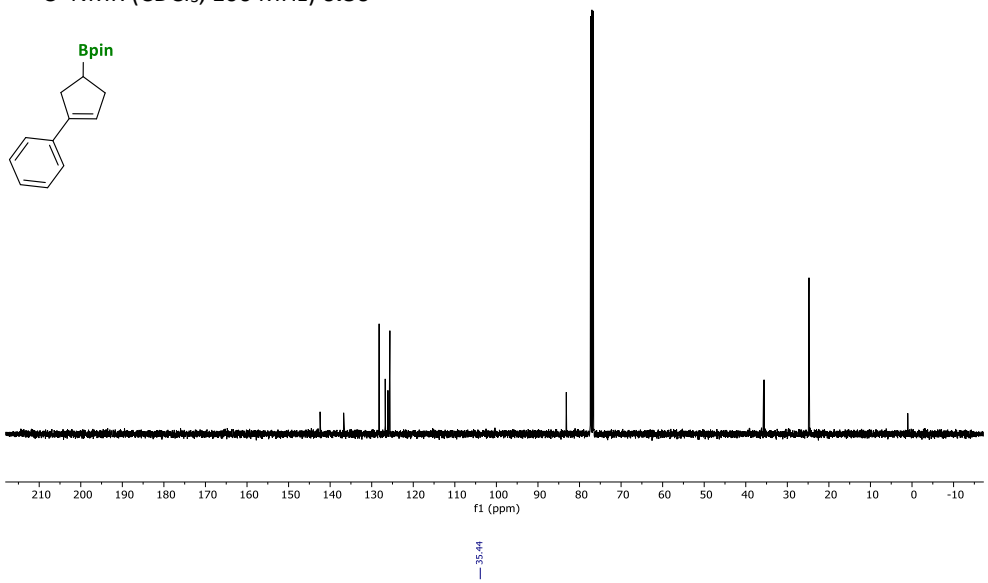
^{1}H- NMR ($CDCl_3$, 400 MHz) **6.30**



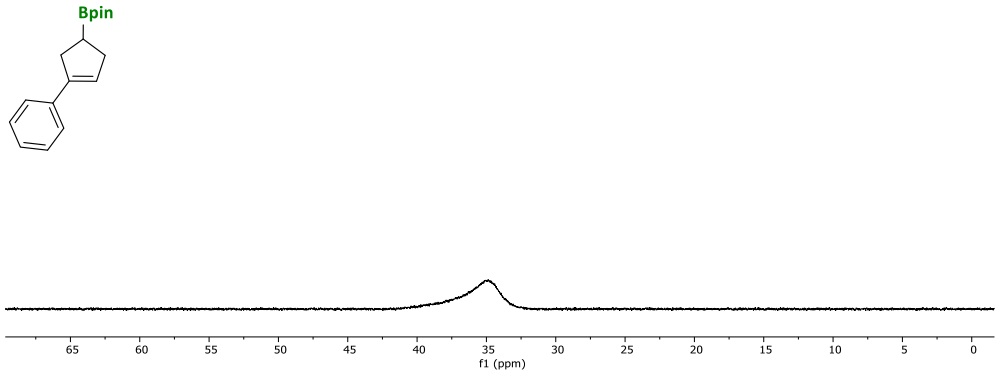




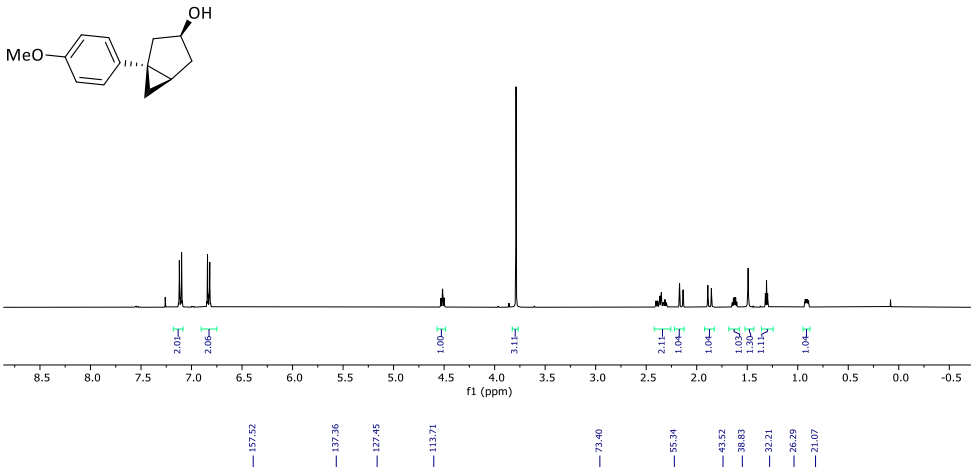
^{13}C- NMR ($CDCl_3$, 100 MHz) **6.30**



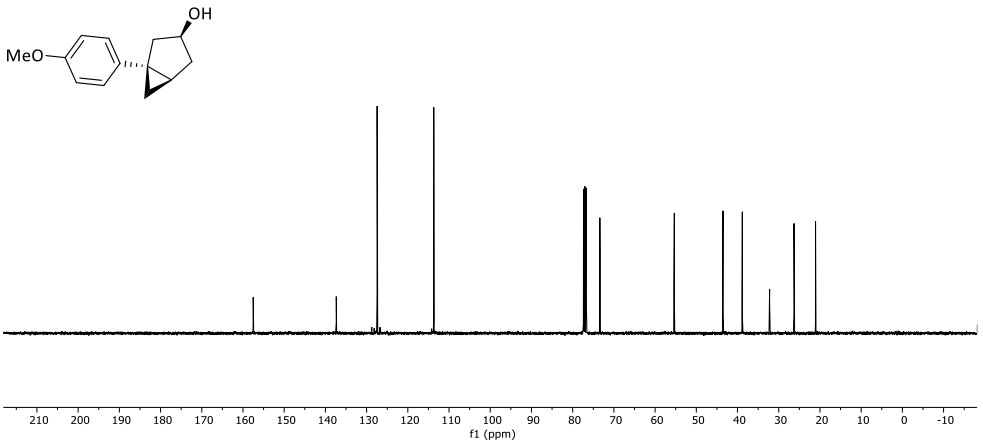
^{11}B NMR ($CDCl_3$, 128.3 MHz) **6.30**



^{1}H- NMR ($CDCl_3$, 400 MHz) **6.56**



^{13}C- NMR ($CDCl_3$, 100 MHz) **6.56**



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[19] Geometry optimisations, transition state searches, and energy evaluations were performed with Gaussian 16 package. The quantum mechanics calculations were performed within the framework of Density Functional Theory (DFT) by using the ωB97X-D functional. For Cu, P, K and I, we employed effective core potentials (ECPs) with double-ζ valence basis set (LANL2DZ), supplemented with polarised shells with the following exponents: Cu (f = 3.525), P (d = 0.387), K (d = 1.000) and I (d = 0.289). For all other atoms, the 6-31G(d) basis set was used. Solvent effects of THF were included using the implicit solvation model SMD. Free energies were computed at a concentration of 1 M and a temperature of 298.15 K.

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Paula Dominguez Molano

CHAPTER VII

Concluding remarks

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Concluding remarks

The present doctoral thesis has successfully developed chemical methodologies through new reactivities and applications. The specific conclusions of the different chapters are described below:

In Chapter III, it has been demonstrated the stereospecific exchange of boryl groups between alkenylboranes and diverse symmetric and unsymmetric diboron reagents for (*E*)-1,2-, (*Z*)-1,2-, 1,1-, and 1,1,2-substituted alkenylboranes, leading to the formation of mixed diboranes. Mechanistic studies suggested that the mechanism involved catalytic activation of the diboron by an alkoxide, which was produced either from a base or the alcohol solvent. With this method established, the introduction of chiral boryl moieties in alkenylboranes has been demonstrated to be a feasible process.

In Chapter IV, the stereoselective cyclopropanation of unsymmetrical 2-aryl-1,1-diborylalkenes with (trimethylsilyl)diazomethane has been investigated using catalytic [$Pd(OAc)_2$]. This process exclusively produced *gem*-bis(pinacolboryl)cyclopropanes, with the silyl and aryl groups in a *trans* configuration. The activation of these polyfunctionalised *gem*-diborylcyclopropanes with NaO^tBu, preferentially promoted protodeboronation on the Bpin moiety *cis* and the aryl group. Subsequent oxidation enabled the synthesis of stereoselective substituted cyclopropanols with high enantioselectivities.

In Chapter V, a conceptually novel 1,3-B/Cu shift has been developed based on a remote rearrangement between $C(sp^2)$–Bpin and $C(sp^3)$–Cu fragments, generated through borylcupration of borylated skipped (*Z*)-dienes. This unprecedented carbon-to-carbon boryl migration occurred with stereospecificity around the alkene, facilitating subsequent stereoselective electrophilic trapping by *in situ* addition of H^+, alkyl halides, allyl halides, I_2, NBS, or NCS. Mixed diborated products could be synthesised via transborylated skipped (*Z*)-dienes. Additionally, the synthetic utility of the novel homoallyl diborated products was explored through palladium-catalysed regioselective cross-coupling, yielding alkylidenecyclohexanes and alkylidenecyclobutanes. The latter were highly strained, yet stable molecules found in biologically active natural products. DFT studies carried out by Prof. J. J. Carbó and co-

workers, highlighted the role of the base in the catalytic activity. It indicated that the 1,3-B/Cu shift occurred via nucleophilic attack of the copper-alkyl moiety on the boron atom bonded to C(sp^2), forming a four-membered boracycle. Copper then migrated to C(sp^2) as the B–C(sp^2) bond opened, resulting in an alkenyl copper intermediate.

In Chapter VI, it has been developed a method for a 1,4-boryl copper shift without the assistance of a heteroatom through the remote 1,4-carbon-to-carbon boryl migration. Using CuCl/Xantphos, the borylcupration of borylated skipped (*E*)-dienes produced diborated terminal compounds, unexpectedly involving the migration of the Bpin group from $C_1(sp^2)$ to $C_4(sp^3)$. This unprecedented carbon-to-carbon boryl migration occurred with stereospecificity around the alkene and enabled subsequent stereoselective electrophilic trapping by the *in situ* addition of H^+, I_2, or NBS. Additionally, it has been applied the novel diborylated (*E*)-iodo substituted alkene to synthesised functionalised cyclopentenes via palladium-catalysed regioselective coupling. This was complemented by strategic cyclopropanation using the OH-directed Simmons-Smith reaction, yielding stereoselective, structurally valuable bicyclic systems. DFT calculations carried out by Prof. J. J. Carbó and co-workers, indicated that the 1,4-B/Cu shift involved a nucleophilic attack of the copper-alkyl moiety on the boron atom bonded to the C(sp^2), forming a five-membered boracycle. This boracycle could then be electrophilically trapped, completing the 1,4-migration. This study also included two opposing effects: the five-membered ring transition state of the 1,4-B/Cu shift was less strained than that of the 1,3-B/Cu shift, but the endo-alkene configuration in the 1,4-B/Cu shift destabilised the cyclic structure. Consequently, the 1,4-B/Cu shift was predicted to involve an exo-alkene moiety that would be more kinetically favourable.

CHAPTER VIII

Summary

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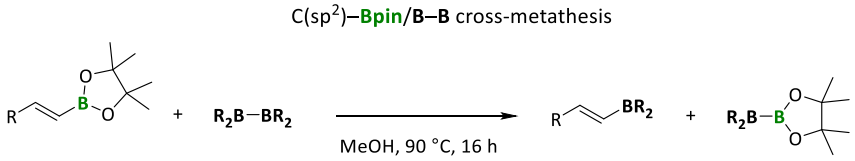
Summary

Over the past decades, organoboron chemistry has garnered significant attention due to its critical role in organic synthesis. Organoboron compounds are highly efficient synthetic tools, capable of being converted into a wide variety of functional groups. *Gem*-diborylalkenes compounds have emerged as promising bifunctional reagents for selective C–C bond formation.

This thesis contributed to the field by introducing new methodologies to synthesise alkenyl boronic esters and *gem*-diborylalkenes and exploring novel activation modes and reactivity trends to create unprecedented organoboron compounds.

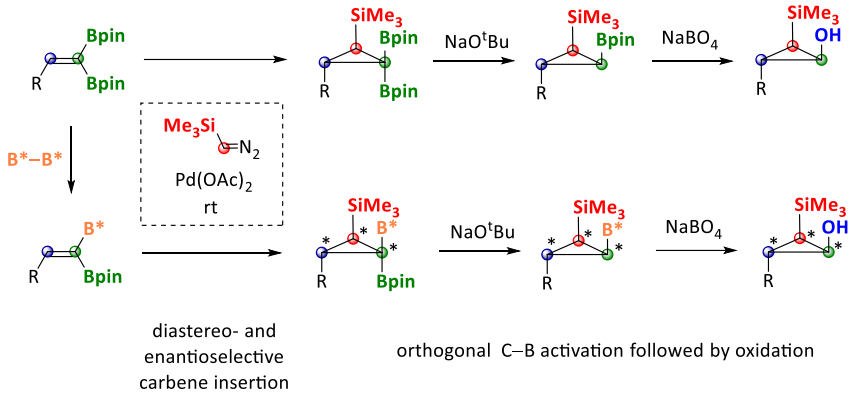
In Chapter III, it was studied the transborylation reaction throughout the stereospecific exchange of boryl groups between alkenylboranes and several symmetric and unsymmetric diboron reagents. The transborylation has been demonstrated for (*E*)-1,2-, (*Z*)-1,2-, 1,1-, and 1,1,2-substituted alkenylboranes, resulting in the formation of mixed diboranes. Mechanistic studies indicated that this process involved the catalytic activation of the diboron by an alkoxide, which was generated either from a base or the alcohol solvent. This established method also facilitated the introduction of chiral boryl moieties into alkenylboranes, representing a straightforward method to prepare chiral alkenylboranes.



Scheme 8.1. Transborylation reaction of alkenylboranes with diboron reagents.

In Chapter IV, the stereoselective palladium-catalysed cyclopropanation of unsymmetrical 2-aryl-1,1-diborylalkenes with (trimethylsilyl)diazomethane has been investigated. This process exclusively produced *gem*-bis(pinacolboryl)cyclopropanes, with the silyl and aryl groups in a *trans* configuration. Activation of these polyfunctionalised *gem*-diborylcyclopropanes with NaO^{t}Bu, in the absence of any transition metal, preferentially promoted protodeboronation on the Bpin moiety *cis*

to the aryl group. Subsequent oxidation allowed for the synthesis of stereoselectively substituted cyclopropanols with high enantioselectivities.

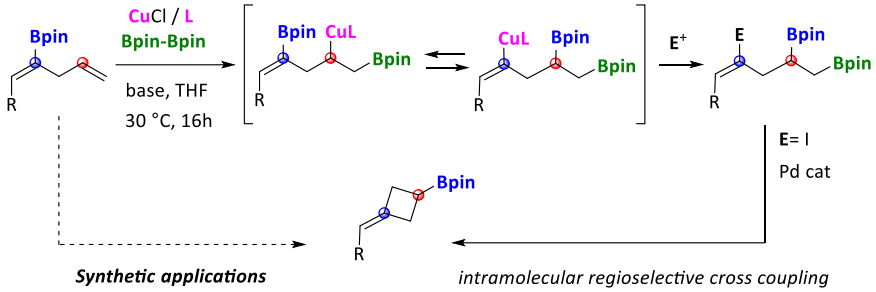


Scheme 8.2. Cyclopropanation reaction of transborylated alkenylboranes.

Furthermore, the borylation of π-systems is an exceptionally versatile method for introducing new functionalities. In this context, copper complexes have proven to be effective catalysts towards the addition of boryl moieties into π-unsaturated systems. These complexes enhanced the nucleophilicity of boryl groups under homogeneous catalytic conditions. This doctoral thesis has contributed to expanding the field through new methodologies that give access to unprecedented organoboron compounds with an emphasis on the efficiency of the protocols and the versatility of the products.

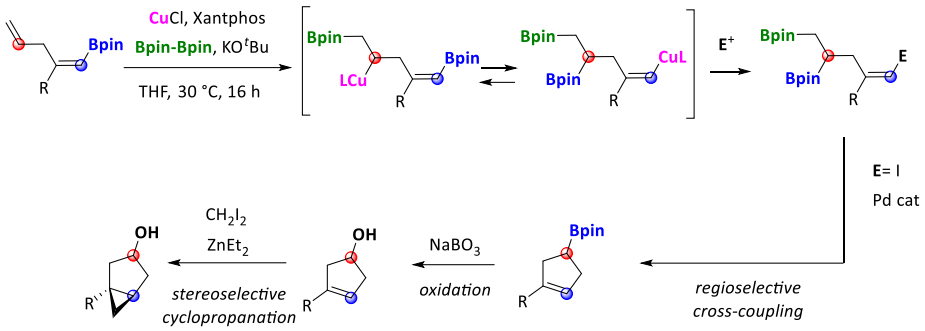
In Chapter V, a study of a new carbon-to-carbon boryl migration has been developed, based on a remote rearrangement between C(sp^2)–Bpin and C(sp^3)–Cu fragments generated through borylcupration of borylated skipped (*Z*)-dienes. This unprecedented boryl migration occurred with stereospecificity around the alkene, enabling subsequent stereoselective electrophilic trapping by *in situ* addition of H^+, alkyl halides, allyl halides, I_2, NBS, or NCS. Mixed diborated products could be synthesised via transborylated skipped (*Z*)-dienes. Furthermore, the synthetic utility of the novel homoallyl diborated products was explored through palladium-catalysed regioselective cross-coupling, yielding alkylidenecyclohexanes and alkylidenecyclobutanes. The latter were highly strained, yet stable molecules found in biologically active natural products. DFT studies carried out by Prof. J. J. Carbó and co-

workers, highlighted the role of the base in catalytic activity, indicating that the 1,3-B/Cu shift occurred via nucleophilic attack of the copper-alkyl moiety on the boron atom bonded to C(sp^2), forming a four-membered boracycle. Copper then migrated to C(sp^2) as the B–C(sp^2) bond opened, resulting in an alkenyl copper intermediate.



Scheme 8.3. Alkenylboranes for 1,3-boron-copper migration reaction.

In Chapter VI, a method for a 1,4-boryl copper shift has been developed, enabling a remote 1,4-carbon-to-carbon boryl migration without the assistance of a heteroatom. Using CuCl/Xantphos, the borylcupration of borylated skipped (*E*)-dienes produced diborated terminal compounds, involving the unexpected migration of the Bpin group from C_1(sp^2) to C_4(sp^3). This unprecedented carbon-to-carbon boryl migration occurred with stereospecificity around the alkene, allowing the subsequent stereoselective electrophilic trapping through the *in situ* addition of H^+, I_2, or NBS. Additionally, the novel diborylated (*E*)-iodo substituted alkene has been used to synthesise functionalised cyclopentenes via palladium-catalysed regioselective coupling. This method was complemented by strategic cyclopropanation using the OH-directed Simmons-Smith reaction, yielding stereoselective, structurally valuable bicyclic systems. DFT calculations carried out by Prof. J. J. Carbó and co-workers, indicated that the 1,4-B/Cu shift involved a nucleophilic attack by the copper-alkyl moiety on the boron atom bonded to the C(sp^2), forming a five-membered boracycle. This boracycle could then be electrophilically trapped, completing the 1,4-migration. The five-membered ring transition state of the 1,4-B/Cu shift was less strained than that of the 1,3-B/Cu shift, but the endo-alkene configuration in the 1,4-B/Cu shift destabilised the cyclic structure. Consequently, the 1,4-B/Cu shift was predicted to involve an exo-alkene moiety, which was more kinetically favourable.



Scheme 8.4. Alkenylboranes for 1,4-boron-copper migration reaction.

List of publications

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