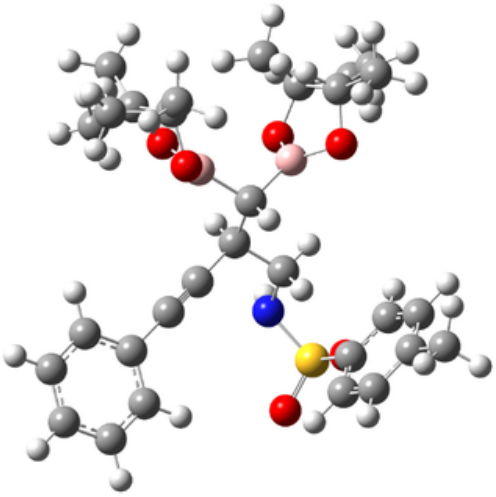
Regioselective ring-opening reaction of propargyl aziridines with diborylalkyllithium salts

BACHELOR'S THESIS



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AGRAÏMENTS

Finalitzen quatre anys de formació, estudi i dedicació contínua. Però, sobretot, finalitza una de les etapes més gratificants i boniques de la meva vida, en la que he tingut la oportunitat i la sort de compartir-la amb gent que per sempre residirà dins meu.

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Com deia a l'inici he tingut la sort de compartir aquest trajecte amb persones que s'han convertit en imprescindibles en la meva vida. Adri, Andreu, Campà, Martin, Chris, Fatima, Jose, Joel, Sergi, Robert, Carlos, Jess, Laura, Lourdes, gràcies per aportar cadascú de vosaltres un granet de sorra en la meva felicitat diària. M'agradaria mencionar-te en especial a tu, Natalia, la meva fidel companya de laboratori i, per sempre, companya de vida. Gràcies per fer-me créixer dia a dia i treure sempre la millor versió de mi.

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Per acabar, aquest treball de fi de grau va especialment dedicat a la meva família. Mama, àvia, avi i Julià (*alies tete)*, per recolzar-me en cadascun dels moments que ha comportat aquest trajecte de quatre anys, siguin bons o dolents. Ens hem demostrat sempre el valor del dia a dia, la importància d'obrir-se a la vida, d'aspirar ben alt i de mai defallir ni decaure tot i les pedres que la vida ens pugui posar pel camí. Us estimo.

Tanco aquests quatre anys feliç. Gràcies a tots i totes!

“Només tens una vida”

Contents

1. Abstract

ENGLISH:

This research work is aimed to gain practical knowledge in the field of catalytic organoboron chemistry, encompassing several essential aspects such as literature review, experimental design, execution of catalytic reactions, product purification, characterization of newly formed organoboron compounds, and analysis of obtained results.

We have studied the diborylalkylation/ring-opening reaction of diverse propargyl aziridines with diborylalkyllithium salts. This study was performed using different steric hindered groups on the *gem*-diborylalkanes to analyze their influence in the reaction outcome and the regioselectivity.

This work opens the perspective towards new ring-opening methodologies of propargyl aziridines allowing access to novel polyfunctionalized amino compounds.

CATALÀ:

Aquest treball de fi de grau està orientat a l'adquisició de coneixement pràctic en el camp de la química organoborada catalítica, considerant diversos aspectes essencials com ara la revisió bibliogràfica, el disseny experimental, l'execució de reaccions catalítiques, la purificació dels productes, la caracterització dels compostos organoborats nous i l'anàlisi dels resultats obtinguts.

Hem estudiat que la reacció de diborilalquilació/obertura d'anell de diverses aziridines propargíliques amb sals de diborilalquil·liti. Aquest estudi s'ha realitzat utilitzant grups amb diferents impediments estèrics en els *gem*-diborilalcans per analitzar la seva influencia en la reacció i la regioselectivitat.

Aquest treball obre perspectives cap a noves metodologies d'obertura d'anell en aziridines propargíliques, permetent l'accés a nous compostos de tipus amino funcionalitzats.

2. Introduction

2.1 Aziridines

2.1.1 Definition of aziridines

Aziridines are three-membered ring amines that are also known as azacyclopropanes, and their use as synthetic scaffolds have recently become a point of interest in organic chemistry.[1] The remarkable reactivity of aziridines is associated with the ring-strain of the three-membered ring, as well as the electron-withdrawing nature of the nitrogen atom.[2] In addition, the presence of substituents, such as vinylic or propargylic groups, on the ring-carbon atom(s) and aryl sulfonyl group on the nitrogen atom, provides a type of aziridines, that are referred to as activated aziridines (Figure 1).[1,2]

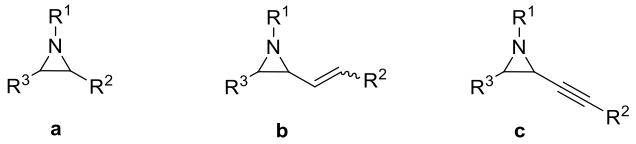


Figure 1: General structure for aziridines (a), vinyl aziridines (b) and propargyl aziridines (c)

2.1.2 General reactivity of propargyl aziridines

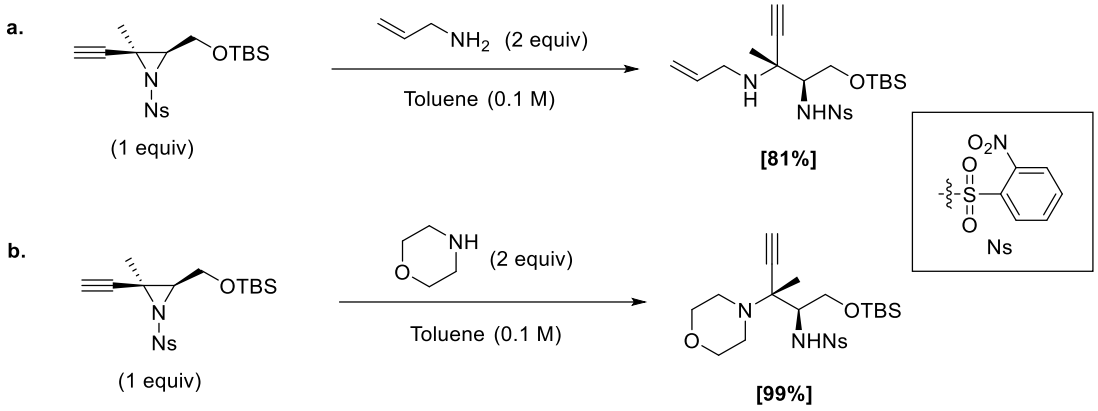
The reactivity of the aziridine ring has been successfully exploited for transformation into diverse types of biologically important compounds.[1] In many cases, the reactions proceed in a highly stereoselective manner to give ring-opening products.[3]

Propargyl aziridines, also known as ethynylaziridine, are electronically characterized by the presence of the triple bond, and the electron-donating or electron-withdrawing influence of the substituents (R_2) attached to it.

The propargyl group provide a reactive site for various transformations, such as cycloadditions, nucleophilic additions and ring-opening reactions. These reactions can form diverse functional groups and complex molecular architectures, making propargyl aziridines valuable intermediates in organic chemistry.

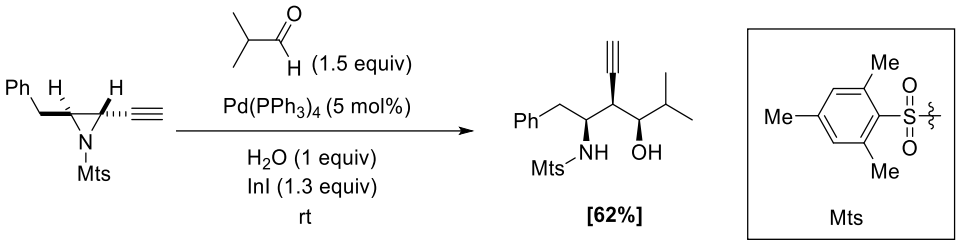
Joullié and co-workers reported the formation of substituted 1,2-diamines *via* nucleophilic ring opening with primary and secondary amines of a chiral trisubstituted propargyl aziridine with complete regio- and stereoselective control.[4]

In this study, several amines with different nucleophilic character were employed. This method allows the formation of unique vicinal diamines while providing a fully substituted carbon center in a stereoselective manner under mild conditions (Scheme 1).[4]



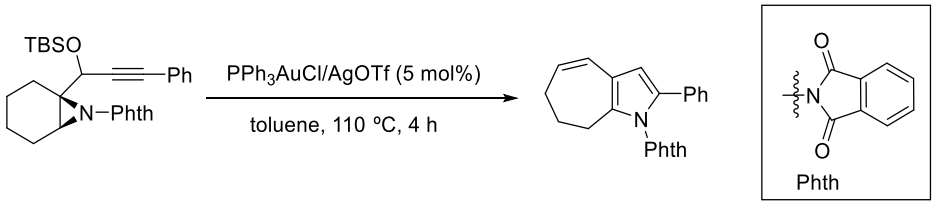
Scheme 1: Nucleophilic Ring-Opening with (a) allyl amines and (b) morpholine

Similarly, Tanaka and co-workers demonstrated the utility of propargyl aziridines as chiral carbon nucleophiles by umpolung with indium(I). The reaction undergoes a palladium-catalyzed reductive coupling of the ethynylaziridine to synthesize 2-ethynyl-1,3-amino alcohol by the treatment of propargyl aziridines with InI, H_2O, catalytic Pd(0) and an optimized solvent (Scheme 2).[5]



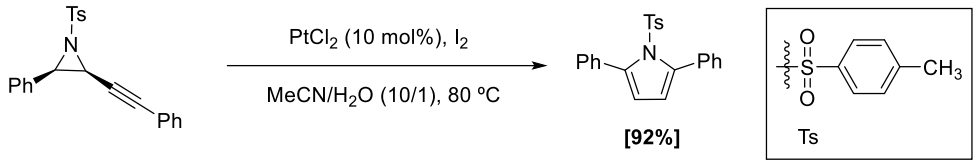
Scheme 2: Reductive coupling reaction of the ethynylaziridine

On the other hand, Zhang and co-workers developed a rearrangement reaction of propargylic aziridine catalyzed by a gold/silver complex. The reaction was performed on a 0.5 mmol scale in 10 mL of toluene with 5 mol% of catalyst at reflux temperature (Scheme 3).[6]



Scheme 3: Au/Ag catalyzed rearrangement reaction of propargylic aziridine

Additionally, Shishido and co-workers developed a methodology based on the electrophilic cyclizations of N-tosyl-substituted propargylic aziridines. The reaction undergoes a platinum ($PtCl_2$) catalyzed cyclization towards the formation of 3-iodopyrroles by the reaction of propargyl aziridine with iodine as an electrophilic reagent (Scheme 4).[7]



Scheme 4: Platinum-catalyzed iodocyclizations of N-tosyl-substituted propargyl aziridines

From this scientific background, the present work will be focus on the study of the ring-opening reactions of N-tosyl-substituted propargyl aziridines, with α-diborylalkyl nucleophiles.

2.2 *Gem*-diborylalkane compounds

2.2.1 Definition of *gem*-diborylalkanes

Organoboron compounds have been widely recognized as versatile intermediates in organic synthesis due to their enhanced stability, non-toxicity, good functional group tolerance, and appropriate properties to the construction of new C-C or C-heteroatom bonds.[8,9]

Among them, *gem*-diborylalkanes can be defined as bifunctional species containing two boryl moieties in geminal position. *Gem*-diborylalkane compounds can conduct selective activation through deborylation or deprotonation and subsequent C-C bond formation.[10] Figure 2 shows different representative examples of *gem*-diborylalkanes with pinacolboryl moieties (Bpin).

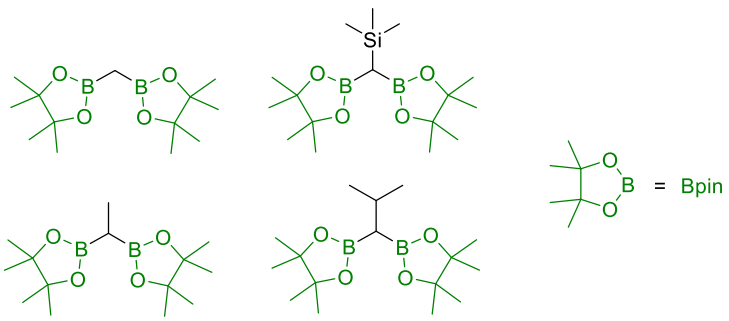
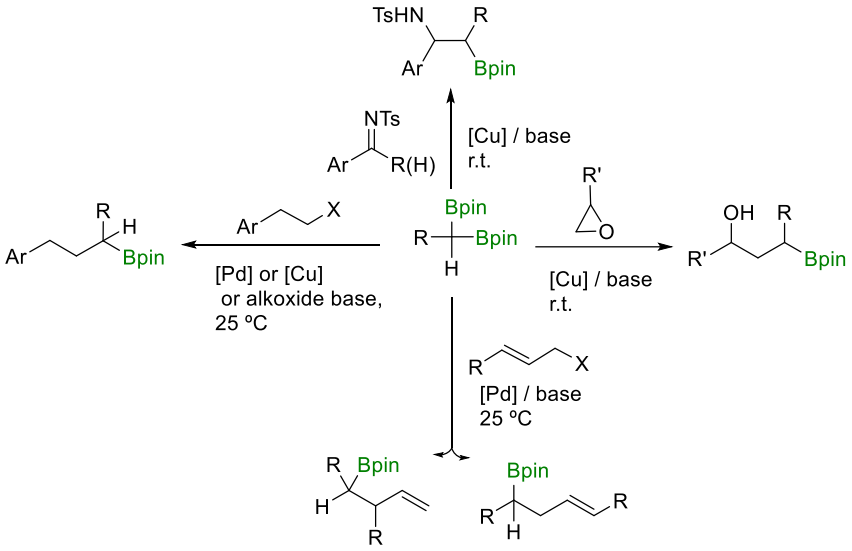


Figure 2: Representative examples of gem-diborylalkanes with pinacolboryl moieties

2.2.2 Reactivity of *gem*-diborylalkanes

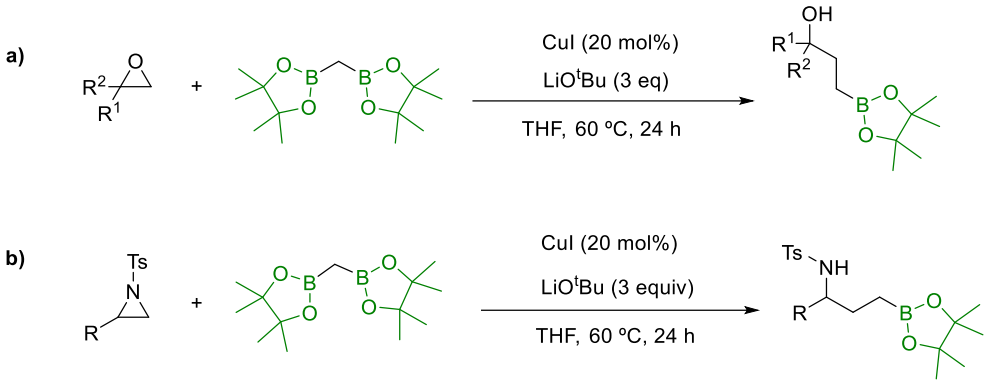
Multiborylated compounds are valuable synthetic intermediates for preparing multifunctionalized molecules. 1,1-Diborylalkanes can be utilized as nucleophilic partners in a variety of chemo-, diastereo- and enantioselective C-C bond-forming reactions by both catalytic and non-catalytic processes (Scheme 5). The alkylation of organic electrophiles using *gem*-diborylalkane reagents has proven to be an important reaction in organic synthesis and most of these reactions proceed through boron-stabilized carbanion intermediates stabilized by the presence of the geminal boryl-group.[11,12]



Scheme 5: Reactivity of 1,1-diborylalkanes towards C-C bond formation[12]

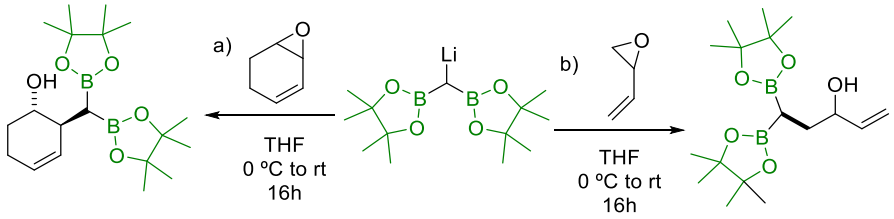
2.2.3 Nucleophilic addition of 1,1-organodiboronates to epoxides and aziridines

Aliphatic, aromatic epoxides as well as aziridines can be converted to the corresponding γ-pinacolboronate alcohols or amines when copper catalyzes epoxide or aziridine ring-opening reaction with *gem*-diborylmethane (Scheme 6a).[13] In addition, N-sulfonyl aziridines were suitable substrates for ring-opening reactions to afford the corresponding γ-amino boronic esters. This newly developed reactions were catalyzed by Cu(I) salts and LiO^tBu base for the borylmethyl alkylation through C-C bond formation. The borylmethylation of substituted 2-alkylaziridines is furnished under mild conditions and the new C-C bond takes place regioselectively on the less sterically hindered carbon (Scheme 6.b).[13]



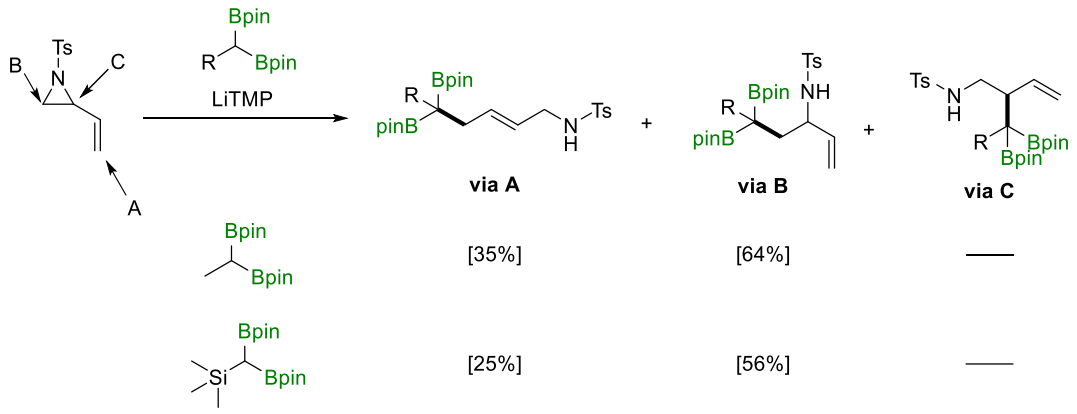
Scheme 6: Copper-catalyzed a) epoxide ring-opening reaction b) aziridine ring-opening reaction with gem-diborylmethane. [13]

Considering the previous work of borylmethylation/ring-opening, Fernández and co-workers[14] studied the S_N2 borylmethylation/ring-opening with vinyl epoxides and styrene oxide with borylmethide lithium salts, taking place in a regio- and diastereoselective way. The nucleophilic ring-opening on 3,4-epoxy-1-cyclohexene was conducted exclusively on the allylic position (Scheme 7a), however the diborylmethide lithium salt reacts with 3,4-epoxy-1-butene at the homoallylic position (Scheme 7b).



Scheme 7: Diborylmethylation/ring opening of a) 2,3-epoxy-1-cyclohexene with LiCH(Bpin)$_2$, b) 3,4-epoxy-1-butene with LiCH(Bpin)$_2$ [14]

Finally, Fernández and co-workers performed a nucleophilic attack on vinyl aziridines with α-diborylalkane lithium bases, generated *in situ* by *gem*-diborylalkanes and LiTMP.[10] 1-Tosyl-2-vinylaziridine was used as model substrate to react with HC(R)(Bpin)$_2$ in the presence of 1.2 equiv of LiTMP. When R = Me, SiMe$_3$, the coupling of LiC(R)(Bpin)$_2$ with the model substrate was principaly formed on the less sterically hindered position via S_N2 pathway, with the S_N2' coupled product as minor product (Scheme 8).



Scheme 8: Diborylalkylation/ring-opening reaction of 1-tosyl-2-vinylaziridine [10]

3. Objectives

The present work is aimed to perform regioselective coupling between diborylalkans and propargyl aziridines, as the main objective.

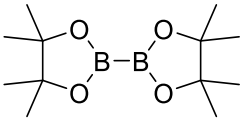
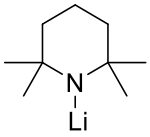
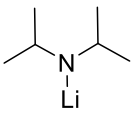
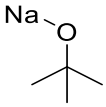
The specific objectives of this work are:

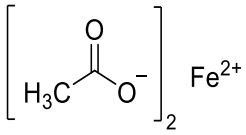
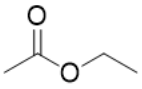
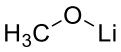
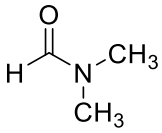
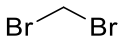
1) Synthesis of diborylalkanes
2) Characterization of diborylalkanes
3) Activation of diborylalkanes with lithium salts and reactivity with propargyl aziridines
4) Study of ring-opening reaction
5) Analysis of reaction products

4. Experimental section

4.1 Reagents and their properties

Table 1: Chemical, properties and safety data[15]

Bis(pinacolato)diboron 	Properties: Solid, melting point: 137-140 °C Protection: lab coat, gloves and glasses 
Lithium 2,2,6,6-tetramethylpiperidide 	Properties: Solid Protection: lab coat, gloves and glasses 
Tetrahydrofuran 	Properties: liquid, density: 0,89 g/cm^3 (at 20 °C), boiling point: 65 °C Protection: lab coat, gloves and glasses 
Lithium diisopropylamide 	Properties: solid Protection: lab coat, gloves and glasses 
Isopropyl bromide 	Properties: liquid, density: 1,31 g/cm^3 (at 25 °C) Protection: lab coat, gloves and glasses 
Sodium tert-butoxide 	Properties: powder Protection: lab coat, gloves and glasses 

Iron(II) acetate 	Properties: solid, melting point: 190 – 200 °C Protection: lab coat, gloves and glasses 
Ethyl acetate 	Properties: solid, melting point: 190 – 200 °C Protection: lab coat, gloves and glasses 
Lithium methoxide 	Properties: beige powder Protection: lab coat, gloves and glasses 
N,N-Dimethyl formamide 	Properties: liquid, clear, boiling point: 153 °C, density: 0,944 g/mL Protection: lab coat, gloves and glasses 
Dibromomethane 	Properties: liquid, clear, boiling point: 96 °C, density: 2,477 g/cm^3 Protection: lab coat, gloves and glasses 
Copper(I) iodide 	Properties: brown powder Protection: lab coat, gloves and glasses 

4.2 General considerations

Solvents and reagents were obtained from commercial suppliers, such as Sigma-Aldrich Inc., Apollo Scientific, Fluorochem, Abcr GmbH, Alfa Aesar, Acros Organics or TCI Chemicals; and were dried and/or purified (if needed) by standard procedures.[16]

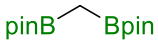
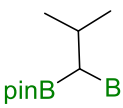
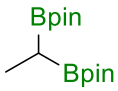
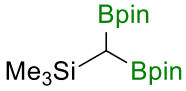
All air-sensitive reactions and procedures were conducted in oven and flame-dried glassware under an inert atmosphere of argon and using Schlenck-type techniques. Flash chromatography purification procedures were performed on standard silica gel (Merck Kiesegel 60 Å, 230 – 400 mesh particle size). Thin Layer Chromatography analyses (TLC) were performed on Merck Kiesegel 60 F_{254} and were developed using standard visualising agents as UV fluorescence (254 and 366 nm) or potassium permanganate and 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 residual signals as reference 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 $BF_3{\cdot}Et_2O$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constants (Hz), Integration). 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 Servei de Recursos Científics i Tècnics of the Universitat Rovira i Virgili, Tarragona or using a BIOTOF II TOF mass spectrometer from Bruker with APCI or EI interface that is located at the Unidad de Espectrometria de Masas e Proteómica of the Univesidad de Santiago de Compostela. GC-MS analyses were performed on a 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.

4.3 General procedure for the preparation of *gem*-diborylalkanes

In this work four *gem*-diborylalkanes have been synthesized using three different strategies. The procedure of synthesis of compounds **1** and **2** follows the reported procedure for the preparation of gem-diborylalkanes.[17]

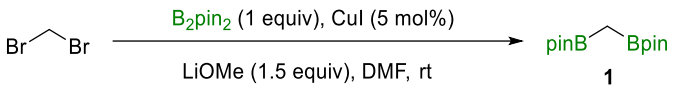
Compound **3** was prepared from the corresponding ester via hydrodiborylation[18] and compound **4** was synthesized via carbene insertion into diborane.[10]

Table 2: Synthesized compounds

Compound 1	Compound 2	Compound 3	Compound 4
			

4.3.1 Synthesis of compounds 1 and 2

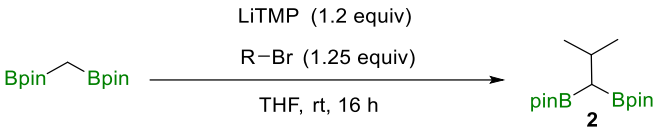
Synthesis of compound 1[17]



*Scheme 9: Synthesis of compound **1***

To an oven-dried 500 mL round-bottom flask were added CuI (1 mmol, 5 mol%), LiOMe (30 mmol, 1.5 equiv) and B_2pin_2 (20 mmol, 1 equiv), then DMF (150 mL) was added under argon and the flask was evacuated and refilled with argon (three times). After stirring at room temperature for 10 min, dibromomethane (20 mmol, 1 equiv) was added via syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, ethyl acetate was added (200 mL). The slurry was filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture in DMF was washed with H_2O and dried over Na_2SO_4, then concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether: ethyl acetate = 50:1) to afford the desired product.

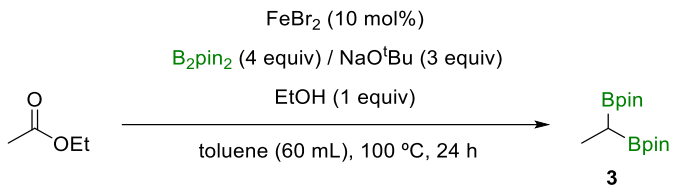
Synthesis of compound 2[17]



*Scheme 10: Synthesis of compound **2***

To an oven-dried 100 mL round-bottom flask were added 1,1-diborylmethane (1 mmol, 1 equiv) and THF (30 mL) and the flask was evacuated and refilled with argon (three times). The reaction mixture was cooled to 0 ℃ for 5 minutes and LiTMP (1.2 mmol, 1.2 equiv) was added dropwise via syringe. After 30 minutes, a solution of alkyl bromide compound in THF (5 mL) was added slowly via syringe. The reaction was conducted for another 30 minutes. Upon completion, saturated ammonium chloride solution was added to quench the reaction, and the reaction mixture was extracted with ethyl acetate, then the organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography to afford the desired *gem*-diborylalkane.

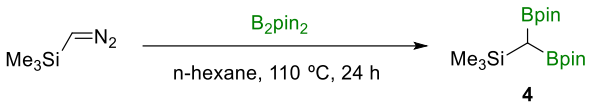
4.3.2 Synthesis of compound 3[18]



*Scheme 11: Synthesis of compound **3***

In the glove box, a flame dried 25 mL Schlenk tube equipped with a magnetic stirrer bar was placed with B_2pin_2 (48 mmol, 4 equiv), NaO^tBu (36 mmol, 3 equiv), $Fe(OAc)_2$ (1.20 mmol, 0.1 equiv) and toluene (2 mL). The reaction flask was sealed with a rubber septum and taken out of the glove box. The mixture was reacted at 100 °C for 1h. After that, the corresponding ester (6 mmol, 1 equiv) and fresh EtOH (0.3 mmol) were added sequentially by syringe and the temperature was maintained at 100 °C with stirring for 12 h. Upon completion, the reaction was quenched by ethyl acetate and water. Aqueous layer was extracted by ethyl acetate (3×15 mL), dried over anhydrous Na_2SO_4 and filtered. The combined organic solvent was removed by using rotary evaporator under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

4.3.3 Synthesis of compound 4[10]



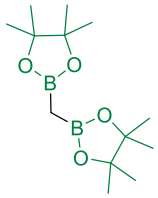
*Scheme 12: Synthesis of compound **4** via carbene insertion into diborane*

In the glove-box, an oven-dried Teflon screw-cap Schlenk reaction flask equipped with a magnetic stir bar was charged with 1 equiv (4 mmol) of bis(pinacolato)diboron. Then 2 equiv (8 mmol) of a 2.0 M solution in hexane of (trimethylsilyl)diazomethane were added dropwise. After stirring the mixture in the glove-box for 5 min the Schlenk flask was sealed and heated at 110 °C for 24 h while constantly stirring. The reaction was cooled at room temperature, the solvent was gently concentrated on a rotary evaporator and the resulting crude purified by silica gel flash chromatography to afford the compound **4**.

The propargyl aziridines used in this work were prepared in the research group of Prof. P. Pérez (University of Huelva), as part of a collaborative project.

4.3.4 Characterization of *gem*-diborylalkanes

Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (1)



1

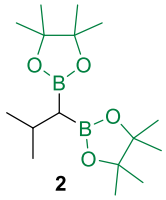
Synthesized using the reported procedure for the preparation of *gem*-diborylalkanes.[17] Purified by flash column chromatography (pentane: diethyl ether = 20:1) isolated as a white solid, in 68% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 24H), 0.34 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 83.1, 82.9, 24.9, 24.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.2.

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



2

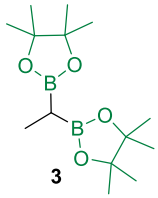
Synthesized using the reported procedure for the preparation of *gem*-diborylalkanes.[17] Purified by flash column chromatography (pentane: diethyl ether = 20:1) isolated as a white solid, in a 63% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10 – 1.97 (m, 1H), 1.23 (s, 12H), 1.22 (s, 12H), 0.95 (d, *J* = 6.5 Hz, 6H), 0.60 (d, *J* = 10.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 82.9, 27.8, 26.6, 25.5, 25.0, 24.6.

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

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



3

Synthesized by the corresponding ester via hydrodiborylation[18] using B_2pin_2 as diboron reagent and purified by flash column chromatography (pentane: diethyl ether = 15:1), isolated as a colourless oil in 59% yield.

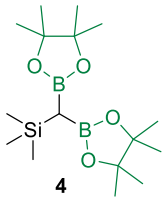
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (s, 6H), 1.19 (s, 18H), 1.02 (d, 3H), 0.69 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 82.8, 24.8, 24.5, 9.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.9.

HRMS (ESI) for **$C_{14}H_{29}B_2O_4^+$[M+H$^+$]$^+$:** calculated: 283.2252, found: 283.2254.

(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane (4)



4

Synthesized via carbene insertion into diborane[10] using B_2pin_2 as diboron reagent and purified by flash column chromatography (pentane: diethyl ether = 15:1), isolated as a white solid in 83% yield.

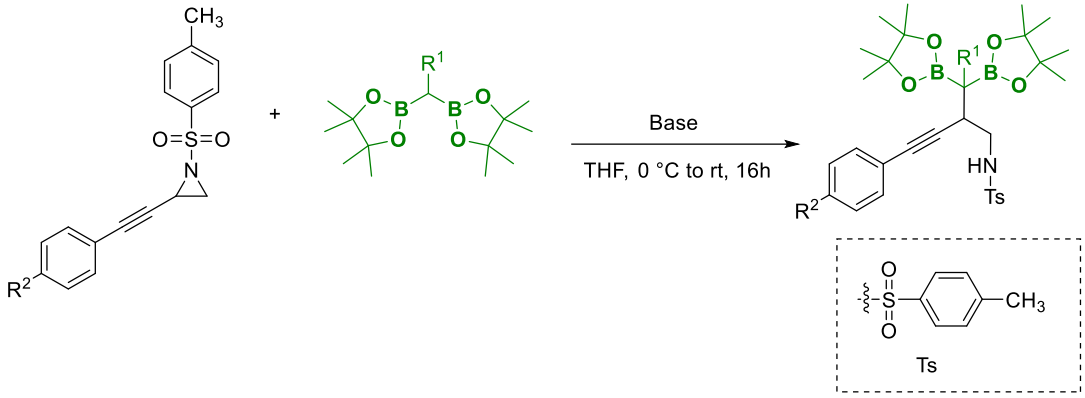
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 12H), 1.20 (s, 12H), 0.28 (s, 1H), 0.09 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 82.7, 25.1, 24.6, 0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.9.

HRMS (ESI) for **$C_{16}H_{34}B_2O_4SiNa^+$[M+Na$^+$]$^+$:** calculated: 363.2310, found: 363.2309.

4.4 General procedure for the ring-opening reaction of propargyl aziridines

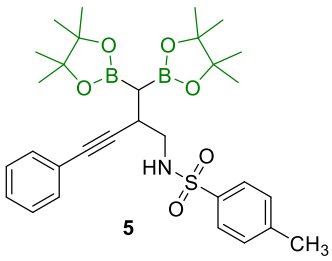


Scheme 13: Regioselective diborylalkylation/ring-opening reaction of propargyl aziridine

In an oven-dried Schlenk-type flask, with a teflon screw cap and a magnetic stirring bar, were added 0.25 mmol (1.25 equiv) of *gem*-diborylalkane. After flushing the flask with Ar for three times, 0.3 mmol (1.5 equiv) of LiTMP were added in the glovebox. The flask was removed from the glovebox and cooled down to 0 °C and 1.5 mL of THF at 0 °C were added at same temperature. The reaction mixture was stirred for 30 minutes at 0 °C After this period of time, 0.2 mmol (1 equiv) of the propargyl aziridine and 0.5 mL of THF were added to the mixture to stir it at 0 °C for 10 minutes. Finally, the reaction mixture was stirred at rt for 16 h. After the reaction time, the solvents were gently evaporated and the crude was purified using silica gel chromatography to afford the corresponding isolated product. This methodology was applied with all the different types of aziridines used during this work.

4.4.1 Characterization of ring-opening products

N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (5)



5

This product was purified by silica gel flash chromatography (pentane: ethyl acetate = 100:10) as white solid (78%, 89 mg).

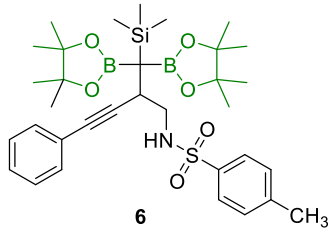
^{1}H NMR ($CDCl_3$, 400 MHz) 7.76 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.19 (m, 7H), 4.97 (m,1H), 3.31 – 3.22 (m, 1H), 3.13 – 2.96 (m, 2H), 2.39 (s, 3H), 1.22 (s, 6H), 1.20 (br, 18), 1.13 (d, *J* = 9.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 137.1, 131.7, 129.7, 128.2, 127.9, 127.3, 123.3, 91.4, 83.7, 83.6, 82.5, 48.1, 29.6, 24.9, 24.9, 24.5, 24.5, 21.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.7.

HRMS (ESI) for **$C_{30}H_{42}B_2NO_6S^+[M+H^+]^+$:** calculated: 566.2918, found: 566.2924.

N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (6)



6

This product was purified by silica gel flash chromatography (pentane:ethyl acetate = 100:10) as pale brownish solid (75%, 96 mg).

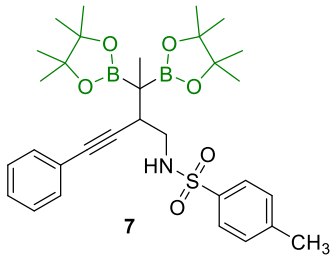
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.3 Hz, 2H), 7.28 (m, 5H), 7.25 – 7.20 (m, 2H), 5.45 (dd, J = 8.9, 3.0 Hz, 1H), 3.53 – 3.49 (m, 1H), 3.44 – 3.32 (m, 1H), 2.86 – 2.80 (m, 1H), 2.38 (s, 3H), 1.24 (s, 6H), 1.19 (s, 6H), 1.18 (s, 6H), 1.16 (s, 6H), 0.09 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 138.1, 131.5, 129.5, 128.3, 127.8, 127.4, 123.8, 92.3, 83.2, 82.9, 47.3, 31.7, 25.5, 25.3, 24.9, 24.8, 24.4, 21.5, 0.05.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.4.

HRMS (ESI) for **$C_{33}H_{50}B_2NO_6SSi^+[M+H^+]^+$:** calculated: 638.3334, found: 638.3321.

N-(2-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (7)



7

This product was purified by silica gel flash chromatography (pentane:ethyl acetate = 100:10) as white solid (74%, 87 mg).

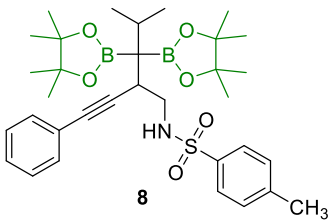
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (m, 5H), 5.05 – 5.00 (m, 1H), 3.30 – 3.21 (m, 1H), 3.16 – 3.03 (m, 2H), 2.39 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 1.18 (s, 12H), 1.15 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 137.1, 131.7, 129.6, 128.2, 127.8, 127.3, 123.4, 90.2, 83.7, 83.6, 83.2, 45.1, 35.5, 24.8, 24.8, 24.7, 24.5, 21.5, 12.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.9.

HRMS (ESI) for **$C_{31}H_{44}B_2NO_6S[M+H^+]^+$:** calculated: 580.3076, found: 580.3081.

4-Methyl-N-(4-methyl-2-(phenylethynyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzenesulfonamide (8)



8

This product was purified by silica gel flash chromatography (pentane:ethyl acetate = 100:10) as white solid (55%, 67 mg).

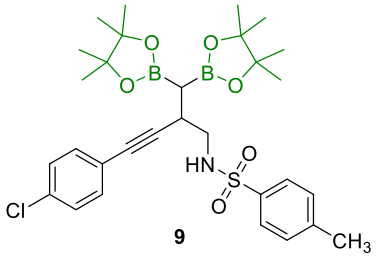
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.18 (m, 7H), 5.28 – 5.21 (m, 1H), 3.55 – 3.45 (m, 1H), 3.30 – 3.20 (m, 1H), 2.93 – 2.88 (m, 1H), 2.37 (s, 3H), 2.22 – 2.12 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.17 (s, 6H), 1.16 (s, 6H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 137.8, 131.6, 129.5, 128.2, 127.8, 127.4, 123.8, 91.1, 83.5, 83.3, 83.2, 46.1, 33.9, 29.9, 25.0, 24.9, 24.9, 24.7, 21.7, 21.5, 21.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.6.

HRMS (ESI) for **$C_{33}H_{48}B_2NO_6S^+[M+H^+]^+$:** calculated: 608.338, found: 608.3394.

N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (9)



9

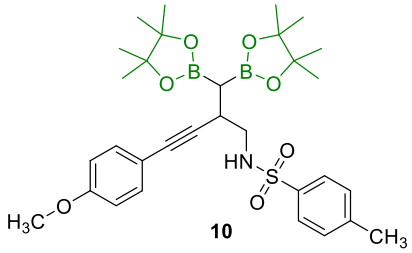
This product was purified by silica gel flash chromatography (pentane:ethyl acetate = 100:10) as white solid (71%, 86 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.26 (m, 6H), 5.01 – 4.92 (m, 1H), 3.34 – 3.24 (m, 1H), 3.13 – 3.01 (m, 2H), 2.42 (s, 3H), 1.24 (s, 6H), 1.22 (s, 6H), 1.22 (s, 6H), 1.21 (s, 6H), 1.14 (d, *J* = 9.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3, 137.3, 133.9, 132.9, 129.7, 128.6, 127.3, 121.9, 92.7, 83.8, 83.6, 81.5, 48.0, 30.4, 29.7, 25.0, 24.9, 24.8, 24.5, 21.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 34.0.

N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (10)



10

This product was purified by silica gel flash chromatography (pentane:ethyl acetate = 100:10) as white solid (68%, 81 mg).

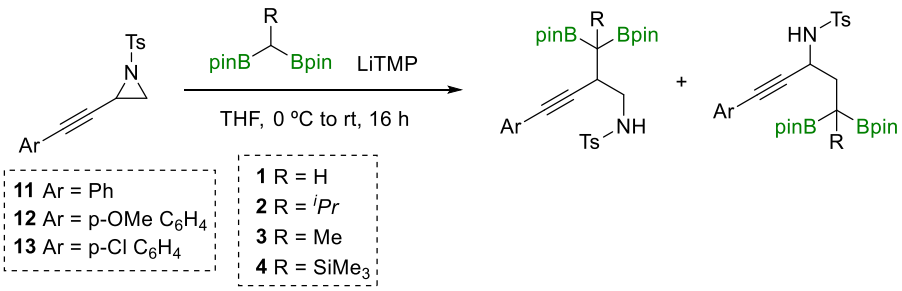
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.21 (m, 4H), 6.83 – 6.75 (m, 2H), 5.00 – 4.92 (m, 1H), 3.79 (s, 3H), 3.29 – 3.22 (m, 1H), 3.10 – 2.95 (m, 2H), 2.40 (s, 3H), 1.21 (s, 6H), 1.19 (s, *J* = 2.2 Hz, 18H), 1.11 (d, *J* = 9.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 143.2, 137.2, 133.1, 129.7, 127.3, 115.5, 113.8, 89.9, 83.7, 83.6, 82.4, 55.3, 48.2, 29.6, 24.9, 24.5, 24.5, 21.6.

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

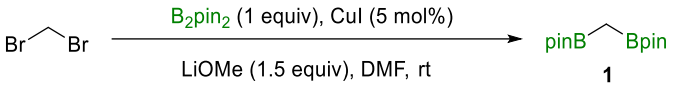
5. Results and discussion

With the main objective in mind, we have studied the ring-opening reaction of propargyl aziridines (**11**-**13**) with different types of *gem*-diborylmethide lithium salts, as nucleophilic agents.



Scheme 14: Ring-opening reaction of propargyl aziridine with the respective gem-diborylalkane

The synthesis of 1,1-diborylalkanes (**1**-**4**) was required. The preparation of bis(4,4,5,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**1**) was based on the use of the general procedure for the preparation of *gem*-diborylalkanes reported by Song and co-workers.[17] This reaction was carried out by using 1 equiv of B_2pin_2 with 1.5 equiv of LiOMe as a base and catalyzed by 5 mol% of Cu (Scheme 15). After the synthetic process, compound **1** was obtained in a 68 % of yield. The full characterization of substrate **1** was conducted through NMR spectroscopy. The ^{1}H NMR spectrum showed the signals at 1.22 ppm corresponding to the eight CH_3 of the pinacolboryl moiety and the signal at 0.34 of the two protons in α position to the boron groups (Figure 3). The NMR data for the compound **1** can be comparable with the NMR described recently in the literature[17] and it was confirmed that we obtained the desired *gem*-diborylalkane.



*Scheme 15: General procedure for the synthesis of compound **1***

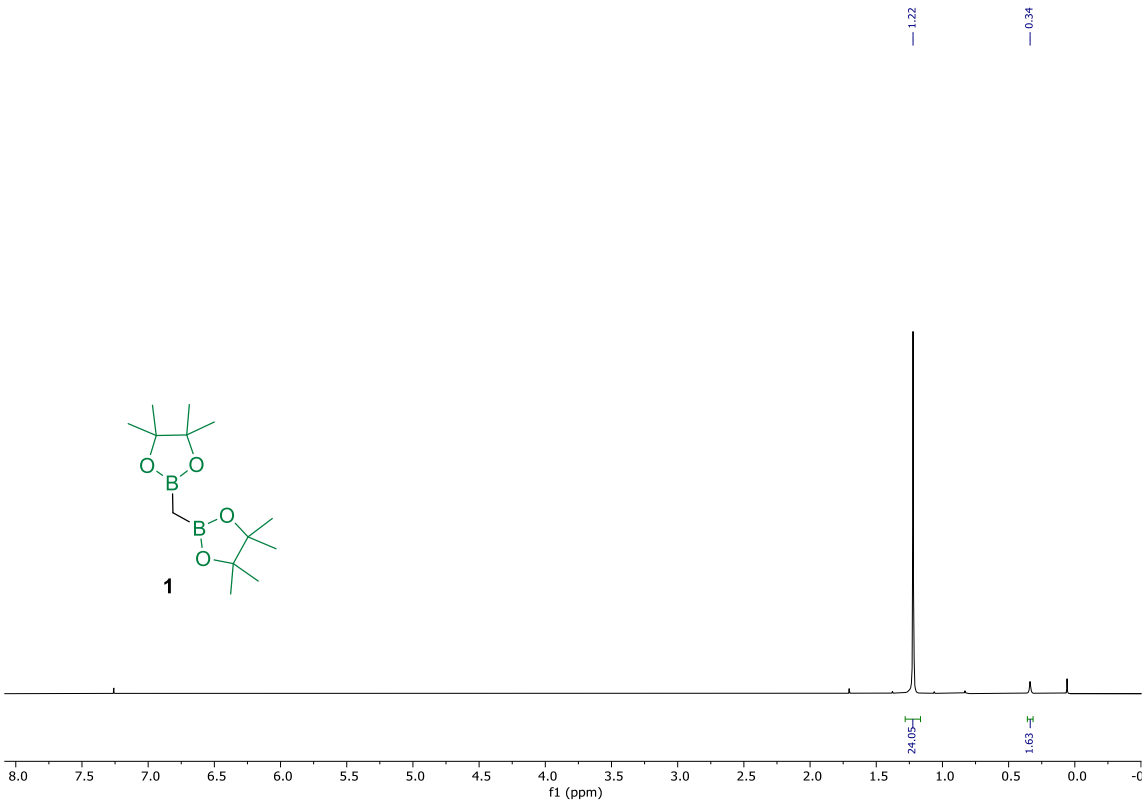
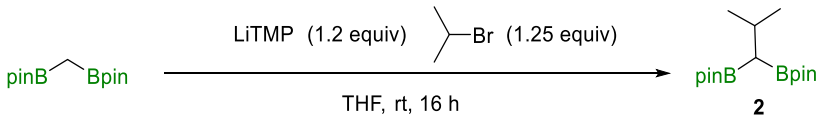


*Figure 3: ^{1}H NMR of compound **1***

Our next objective was the synthesis of the 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2**), which corresponds to the isopropyl substituted *gem*-diborylmethane. Compound **2** was prepared from **1** following a reported methodology (Scheme 16).[17] The reaction was carried out by the addition of 1.25 equiv of isopropyl bromide as an electrophile agent and 1 equiv of B_2pin_2 treated with 1.2 equiv of LiTMP. Compound **2** was obtained with a 63% of yield. The full characterization of **2** was conducted through NMR spectroscopy (Figure 4). The ^{1}H NMR denote the signals corresponding to the two methyl groups of the isopropyl group, appearing in the same doublet signal at 0.95 ppm. In addition, we observe the protons of the methyl groups of the boron moiety at 1.22 and 0.95 ppm, appearing in two singlets. At 2.04 ppm appears the signal corresponding to the remaining proton of the isopropyl group. The ^{1}H NMR spectra obtained is in agreement with the reported at the literature.[17]



*Scheme 16: General procedure for synthesis of compound **2***

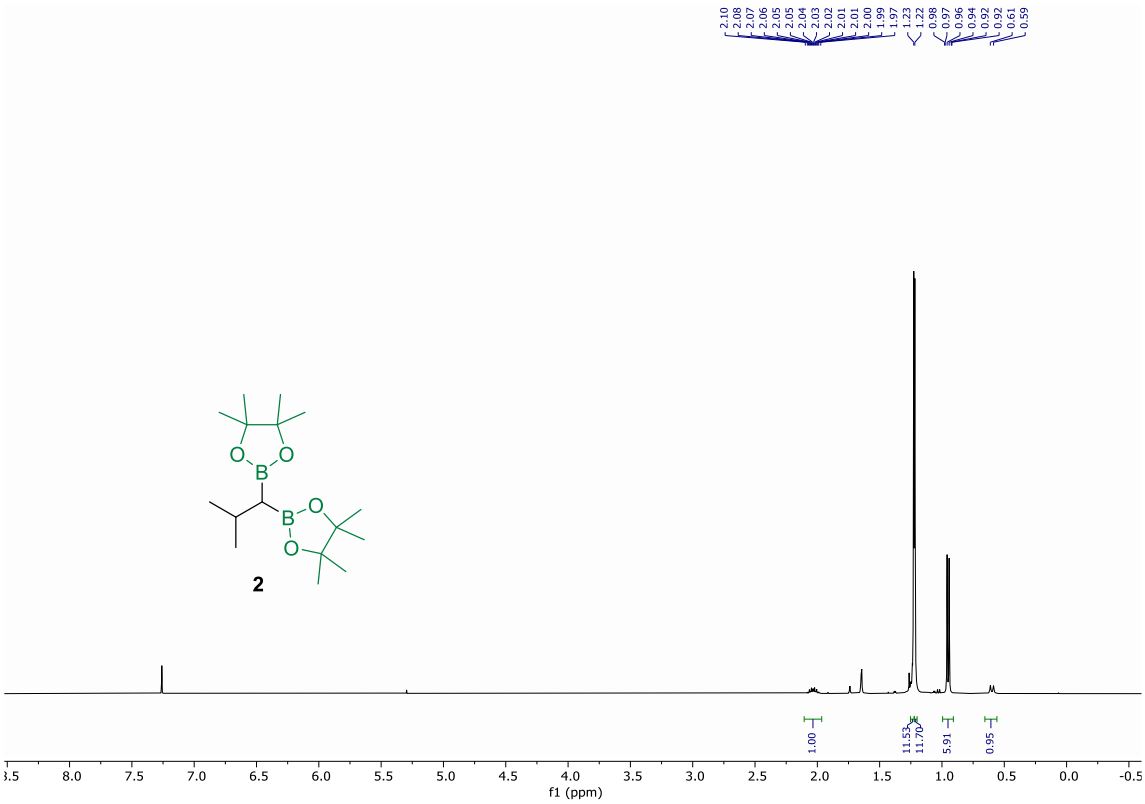
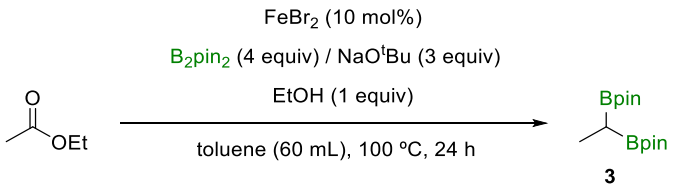


*Figure 4: ^{1}H NMR of compound **2***

Subsequently, we have carried out the synthesis of 2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3**). Interestingly, we learned a methodology based on a hydrodiborylation using B_2pin_2 as diboron reagent and the corresponding ester (Scheme 17). This strategy was reported by Liu and co-workers[18]and compound **3** was obtained in a 59 % of yield and characterized by NMR spectroscopy (Figure 5). The ^{1}H NMR spectrum showed the signals of pinacolboryl moieties in two singlet signals at 1.19 and 1.20 ppm. Next to this, the signal of the proton in α position to the boron groups appears at 0.69 ppm. Finally, there is a signal at 1.02 ppm in a doublet form regarded to the protons of the methyl group. The ^{1}H NMR spectra obtained of substrate **3** is in agreement with the literature.[18]



*Scheme 17: Ester hydrodiborylation methodology for the obtention of compound **3***

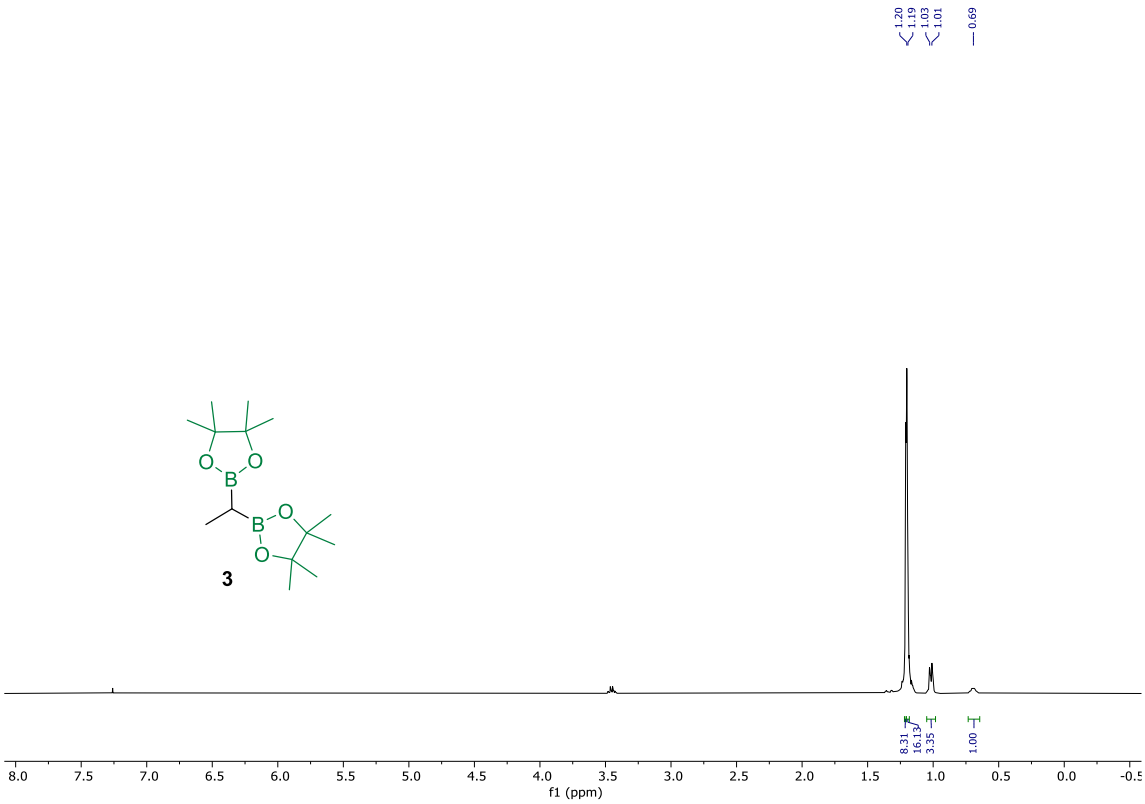
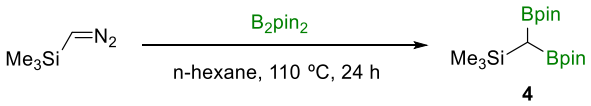


*Figure 5: ^{1}H NMR of compound **3***

Our last *gem*-diborylalkane synthesized was the (bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane (**4**). The strategy followed was reported by Fernández and co-workers and was based on a carbene insertion into diborane (Scheme 18).[10] After the corresponding purification, compound **4** was isolated in an 83% of yield and characterized through NMR spectroscopy comparing the signals with the literature. The ^{1}H NMR spectra depicts the presence of a singlet at 0.09 ppm regarded to the $SiMe_3$ group (Figure 6), as well as the two pinacolboryl moieties at 1.20 and 1.21 ppm.



*Scheme 18: Carbene insertion into diborane for the synthesis of compound **4***

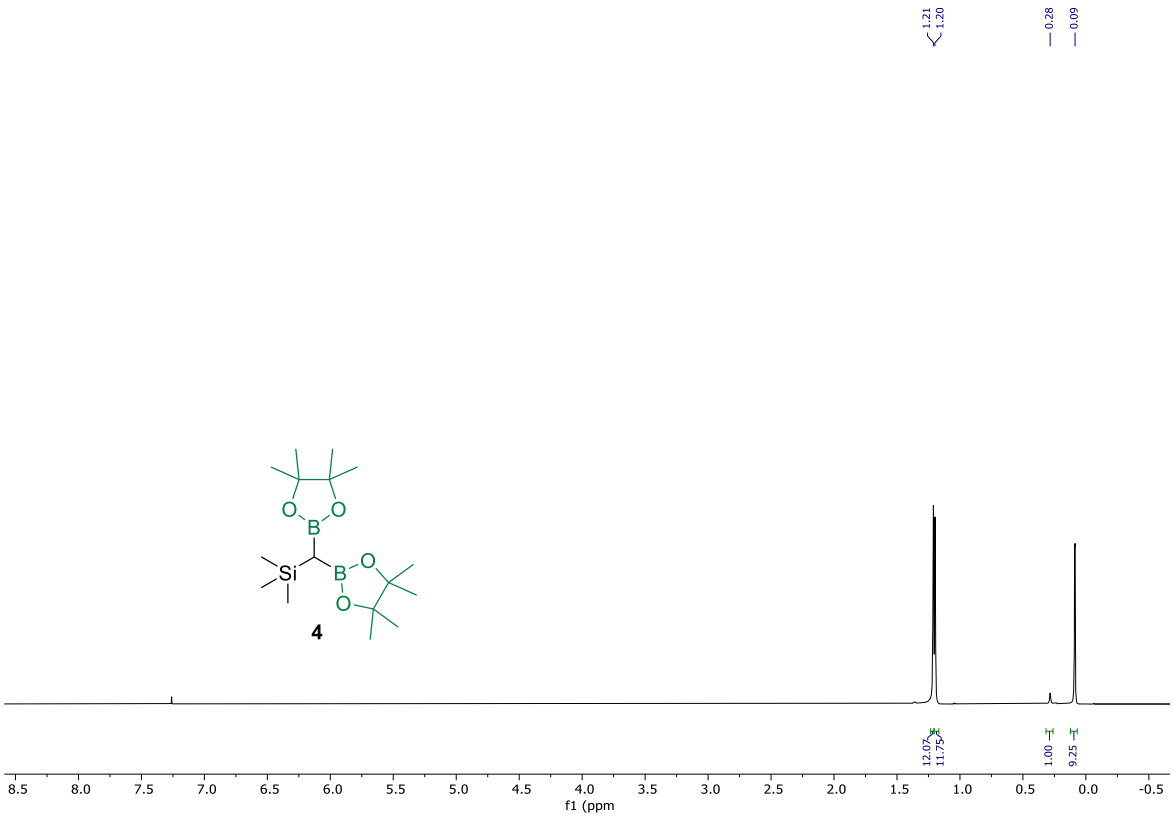
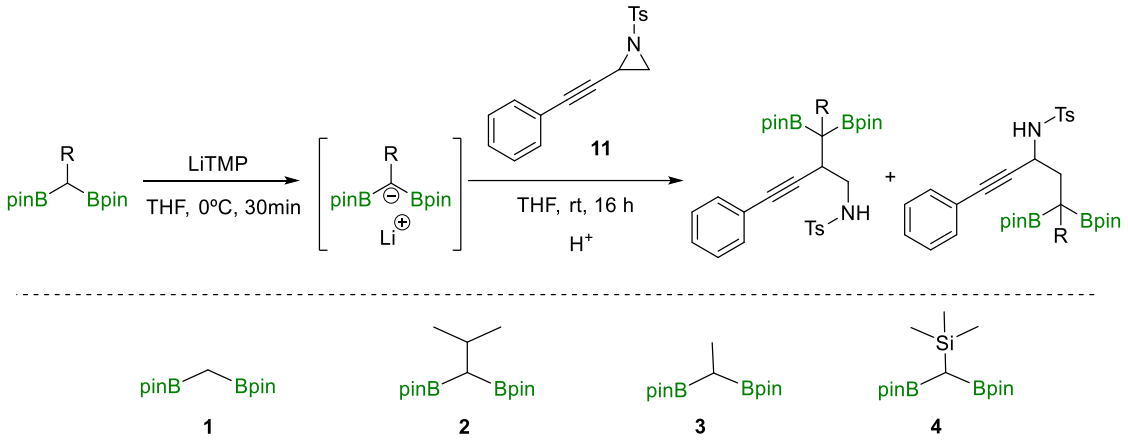


*Figure 6: ^{1}H NMR of compound **4***

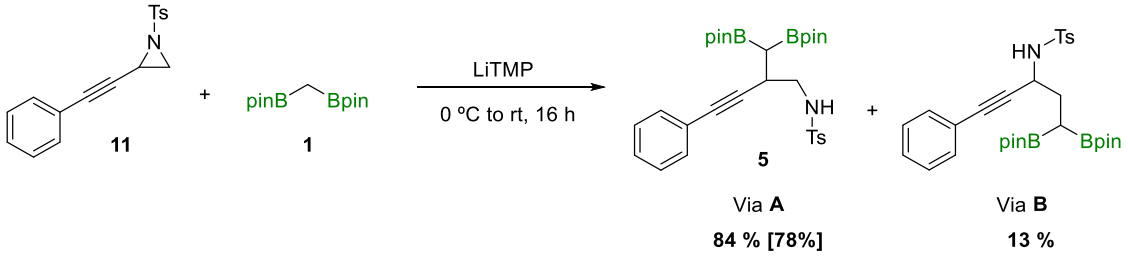
With all the *gem*-diborylalkanes prepared, we next focus to the diborylalkylation via ring-opening reaction using the propargyl aziridine 2-(phenylethynyl)-1-tosylaziridine **(11)** as model substrate to afford versatile propargylic amines. The first step of the ring-opening reaction involves the deprotonation of the *gem*-diborylalkanes to form the corresponding diborylmethide lithium salts.

The activation of diborylalkanes was performed by LiTMP via deprotonation and generation of the corresponding salt. Subsequently, the diborylmethide lithium salt promotes the nucleophilic attack on the corresponding propargyl aziridine and ring-opening occurs, with concomitant protonation as final step (Scheme 19).



*Scheme 19: Ring-opening reaction of propargyl aziridine **11** as a model substrate with diborylalkyllithium salts*

To study the viability of our work hypothesis, the ring-opening reaction was performed using **1** as *gem*-diborylalkane to react with **11** in the presence of 1.5 equiv of LiTMP. When the reaction took place, the model substrate was quantitatively transformed into two products. The major product was **5** (isolated yield 78%) formed via S_N2 diborylalkylation ring opening reaction on the most sterically hindered position (Scheme 20, via A). However, we obtained a competitive by-product which is the minor product formed on the coupling to less sterically hindered position (not isolated product) (Scheme 20, via B). Product **5** has been isolated for the first time in this work and we characterized it via NMR spectroscopy (Figure 7) and HRMS.



*Scheme 20: Ring-opening reaction of model substrate **11** with **1***

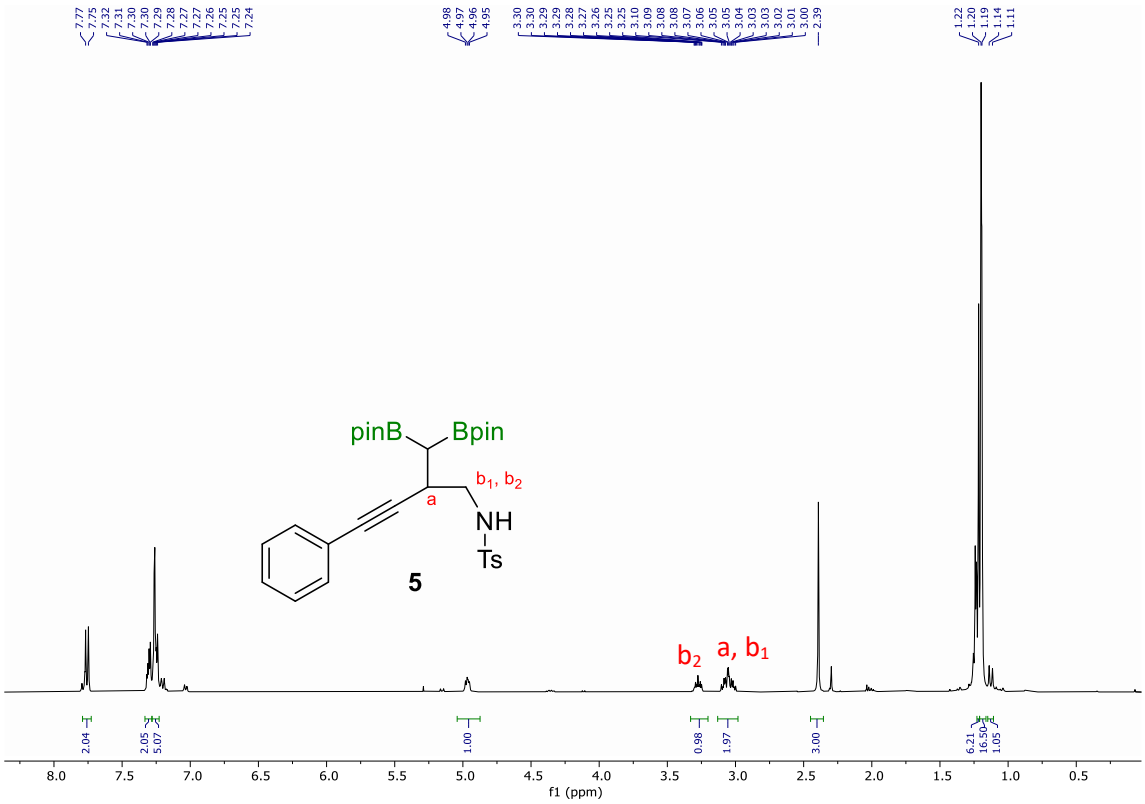
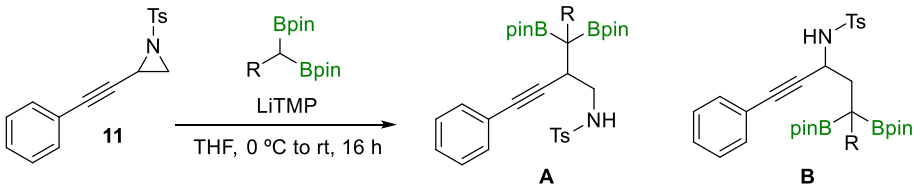
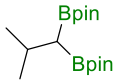
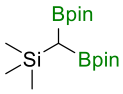


*Figure 7: ^{1}H NMR of ring-opening product **5***

In ^{1}H NMR spectroscopy, we observed multiple signals in the range of 7 – 8 ppm corresponding to the aromatic protons present in the tosyl group attached to the nitrogen and the phenyl group bonded to the triple bond. At 4.97 ppm appears the signal of the amine proton that also indicates that the reaction has been carried out due to the obtention of the amine group. It's important to highlight that for the assignment of the proton a, b_1 and b_2 we performed a COSY-H trying to correlate each proton with the signals appeared in the range of 2.75 – 3.5 ppm. At 2.39 ppm appears the singlet related to the methyl substituent from the tosyl group. Additionally, the protons of the methyl groups of Bpin moieties appears at 1.20 and 1.22 ppm associated in a singlet and a broad signal. The proton in alfa of Bpin groups, is identified at 1.13 ppm as a doublet.

Our next step was the study of the influence of steric hindrance around the α-diboryl carbanion to see if there is different possible ring-opening reactions that can be conducted. Towards this study, we selected the three substituted *gem*-diborylalkanes of molecular formula $HCR(Bpin)_2$ (where R = ^{i}Pr, Me and $SiMe_3$).



Geminal-diborylalkane	Product A	Product B
 2	**8 [45%]**	**[4%]**
 3	**7 [74%]**	**[4%]**
 4	**6 [75%]**	**[7%]**

*Scheme 21: Ring-opening reaction of **11** with substituted gem-diborylalkanes*

In all cases, we can observe a similar behaviour among all the *gem*-diborylalkanes and most of the formed products were isolated as a result of nucleophilic attack at the most congested position of the propargyl aziridine (Scheme 21, ring-opening product A). Furthermore, there is a slight tendency towards nucleophilic attack on the less sterically hindered position (Scheme 21, ring-opening product B). All the ring-opening products were isolated for the first time in this work. Focusing on the development of the reaction for compound **4**, we observed that the steric hindrance present in the *gem*-diborylalkanes was not a limiting factor in the ring-opening reaction. The product **6** of the ring-opening reaction on the most electrophilic position was observed as major product and was isolated in a 75% of yield (Scheme 21). Additionally, the reaction occurred also on the less sterically-hindered position of the aziridine in a 7% of yield (Scheme 21). The characterization of compound **6** was conducted and ^{1}H NMR spectrum is showed in Figure 8.

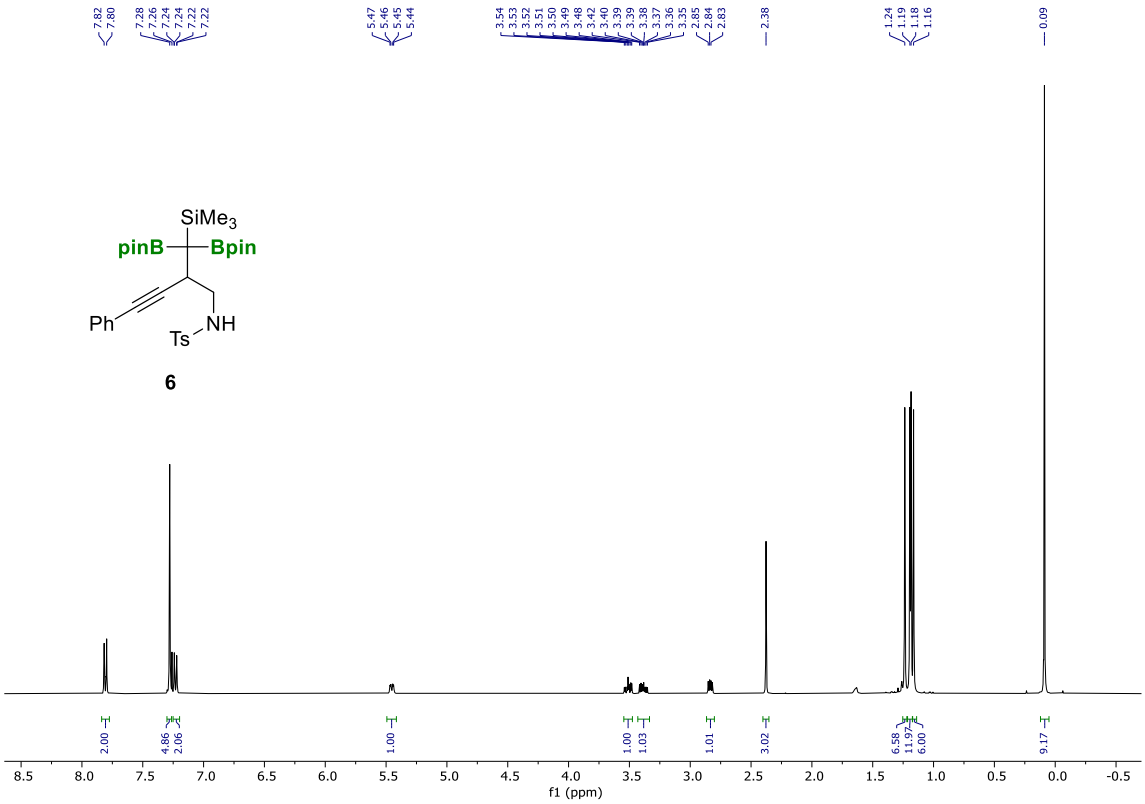
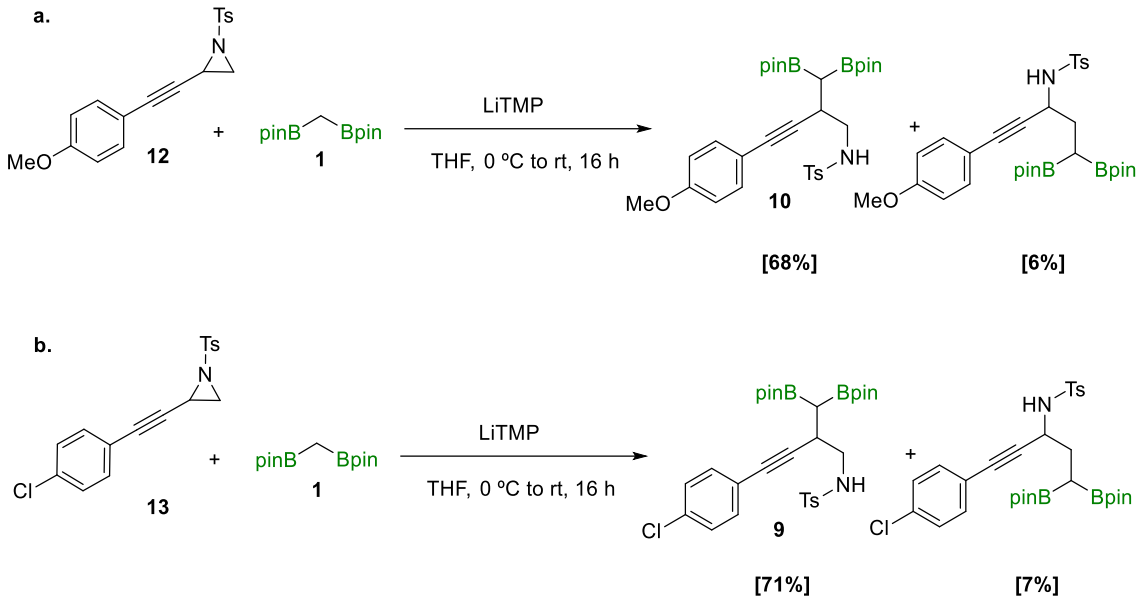


*Figure 8: ^{1}H NMR of ring-opening product of compound **4***

Once we performed the study and observed that there was compatibility with the steric hindrance of *gem*-diborylalkane, our next focus on the project was to study the reactivity of different propargyl aziridines with electron-withdrawing and electron-donating groups on *para* position at the phenyl group. To conduct the experiments, we suggested 2-((4-methoxyphenyl)ethynyl)-1-tosylaziridine (**12**), which contains an electro-donating methoxide group (Scheme 22a), and 2-((4-chlorophenyl)ethynyl)-1-tosylaziridine (**13**), with an electron-withdrawing chlorine group as strategic aziridines for the study (Scheme 22b). We performed the reactions of ring-opening with the simplest compound **1** as ring-opening partner in the presence of LiTMP (Scheme 22). The characterization of the products **9** (Scheme 22b, Figure 10) and **10** (Scheme 22a, Figure 9) was conducted through NMR spectroscopy. Both products have a similar set of signals in the ^{1}H NMR spectrum, however product **10** also is characterized by the OCH_3 signal at 3.79 ppm.



*Scheme 22: Ring-opening reaction of a. **12** and b. **13** with gem-diborylalkane **1***

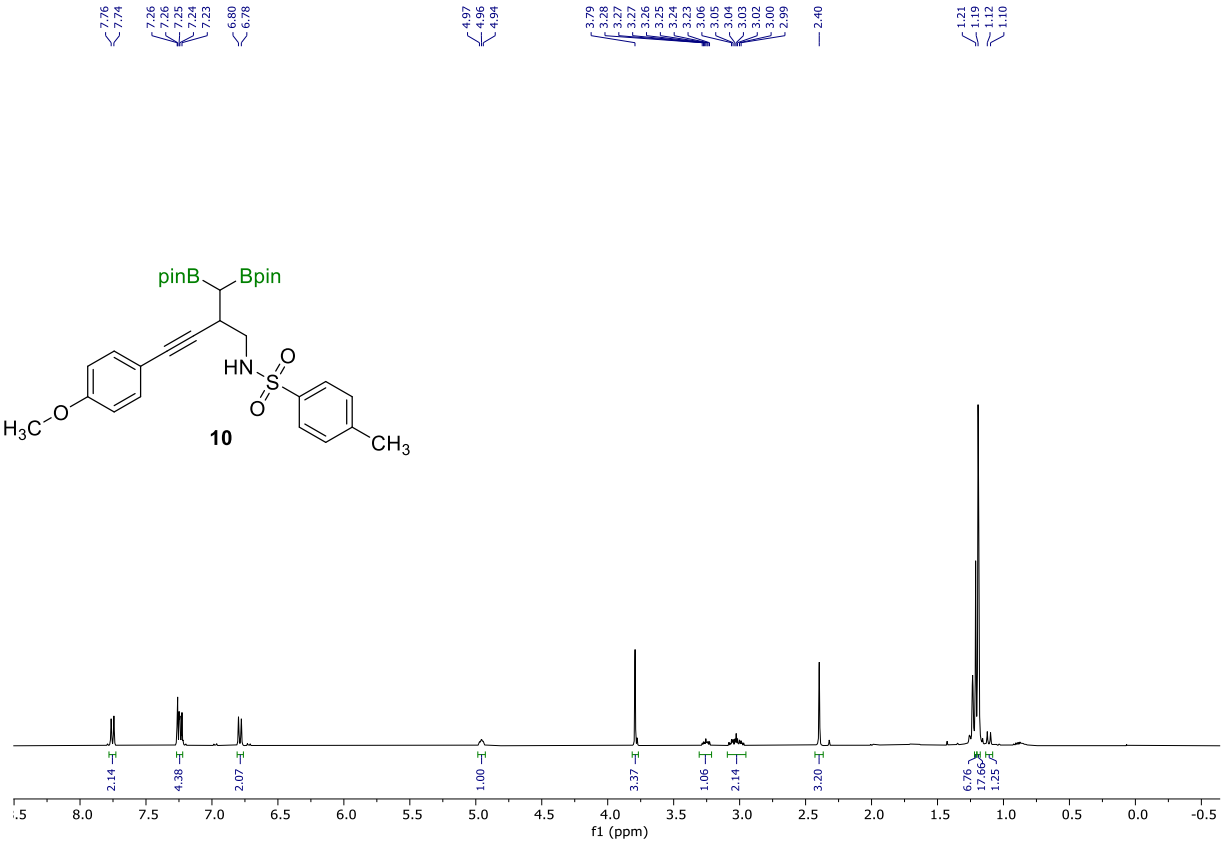


*Figure 9: ^{1}H NMR of product **10***

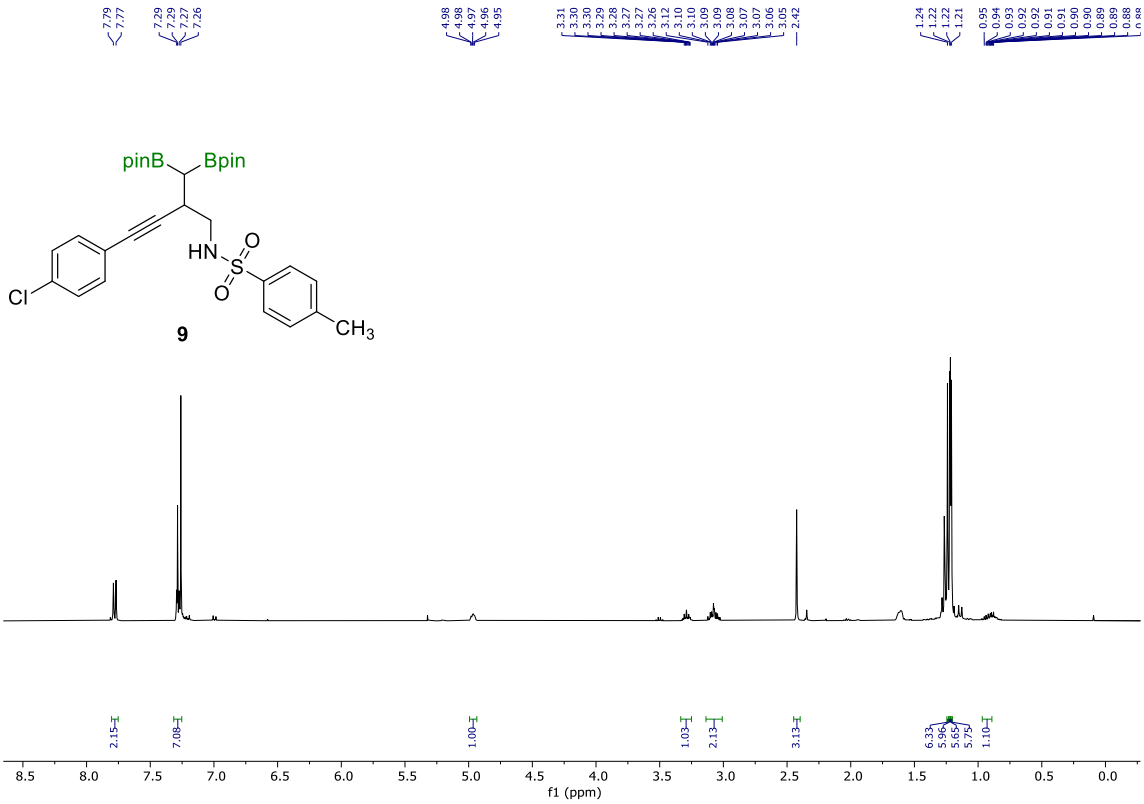


*Figure 10: ^{1}H NMR of product **9***

Looking at the results, we observed that the presence of an electron-donor or an electron-withdrawing group on *para* position of the phenyl moiety didn't cause any change in the regioselectivity of the reaction suggesting that nucleophilic attack to propargyl aziridines has a favoured coupling at the most hindered and electrophilic position despite the electronic nature of the aryl groups.

For future projections, we could consider the possibility to prepare a propargyl aziridine with alkyl substituents on the most hindered position, to block that electrophilic carbon, promoting the coupling with the less hindered position.

6. Conclusions

ENGLISH: To conclude, it is important to mention that the objectives planned for this work have been accomplished.

- Four different *gem*-diborylalkanes have been synthesized and characterized
- Diborylmethide lithium salts have been prepared using LiTMP and geminal diborylalkanes for the concomitant reactivity with propargyl aziridines.
- Six new coupling compounds have been synthesized and characterized for the first time.
- Optimization of the reaction conditions towards regiocontrol of the nucleophilic attack, have been developed.

In particular, it has been observed that propargylic aziridines react with diborylmethide lithium salts *via* a regioselective manner, suggesting a S_N2 mechanism being the predominant coupling at the most electrophilic position. In addition, it has been observed that the reactivity tested with other type of propargyl aziridines, in order to study the influence of electron-donor or electron-withdrawing group in the phenyl moiety of the aziridine, didn't affect to the regioselectivity of the ring-opening reaction. Even so, more studies must be done to completely understand the reactivity of the diborylalkylation/ring-opening reaction of propargyl aziridines.

CATALÀ: Per a concloure, és important esmentar que els objectius planificats per aquest treball s'han completat:

- S'han sintetitzat i caracteritzat quatre diferents *gem*-diborilalcans.
- S'han preparat sals de diborilalquil·liti utilitzant LiTMP i *gem*-diborilalcans per a la reactivitat relacionada amb les aziridines propargíliques.
- S'han sintetitzat i caracteritzat sis nous compostos organoborats, no reportats en la bibliografia.
- S'han optimitzat les condicions de reacció per regiocontrol en l'atac nucleofílic que s'ha desenvolupat.

En particular, s'ha observat que les aziridines propargíliques substituïdes reaccionen amb les sals litiades del corresponent *gem*-diborilalcà de manera regioselectiva, suggerint un mecanisme S_N2 predominant en la posició més electrofílica. A més, s'ha observat que la reactivitat provada amb altres tipus de aziridines propargíliques per estudiar la influència de la presencia d'un grup donador o acceptor d'electrons en el grup fenil de l'aziridina, no afecta a la regioselectivitat de la reacció d'obertura d'anell. Tot i la feina realitzada, cal emprendre més estudis per entendre completament la reactivitat de diborilalquilació/obertura d'anell de les aziridines propargíliques.

7. References

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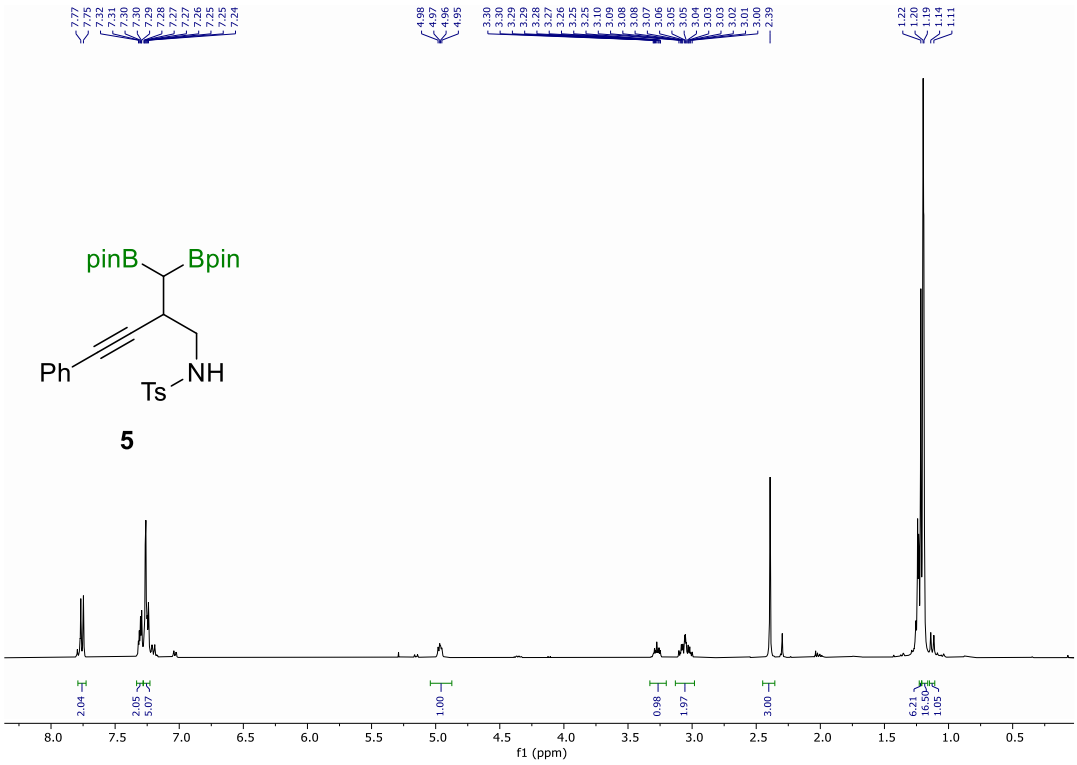
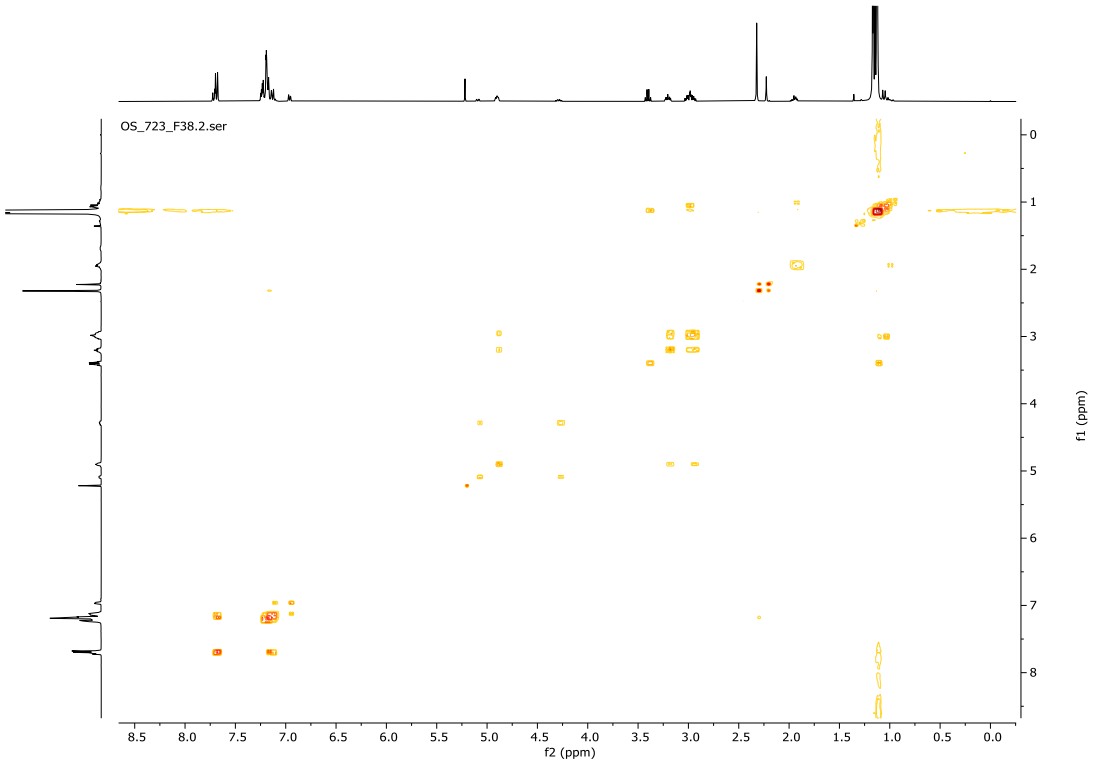
8. Appendix

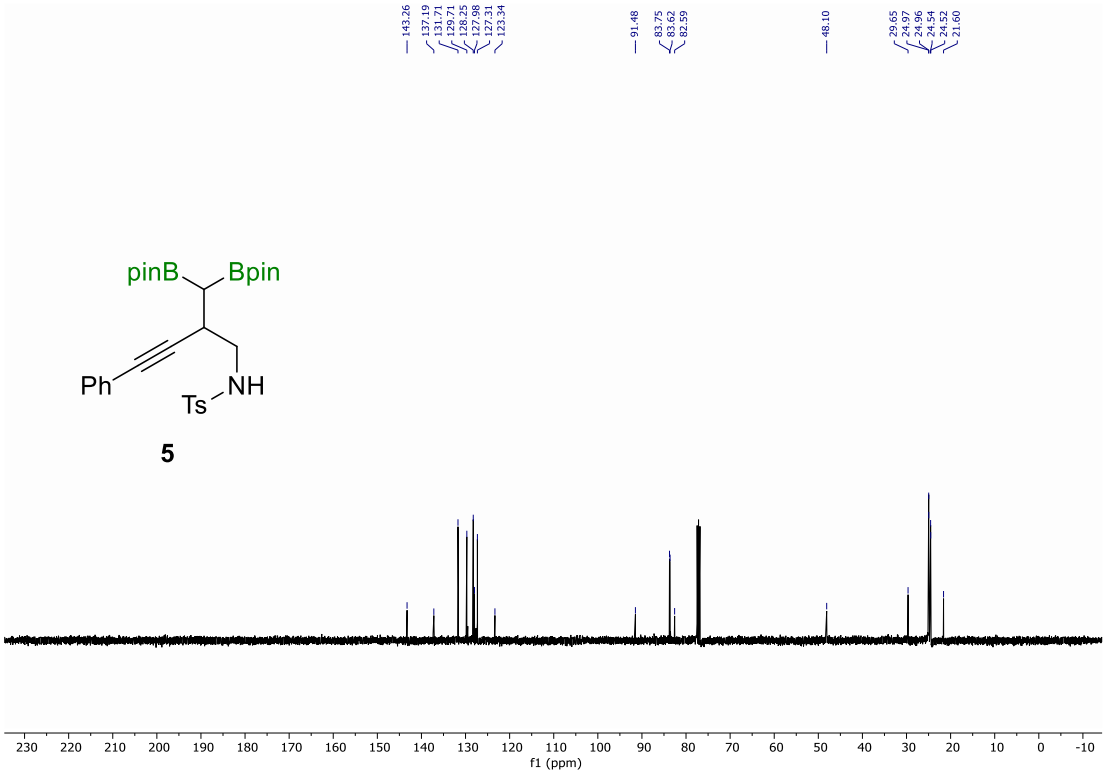
^{1}H NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (5)



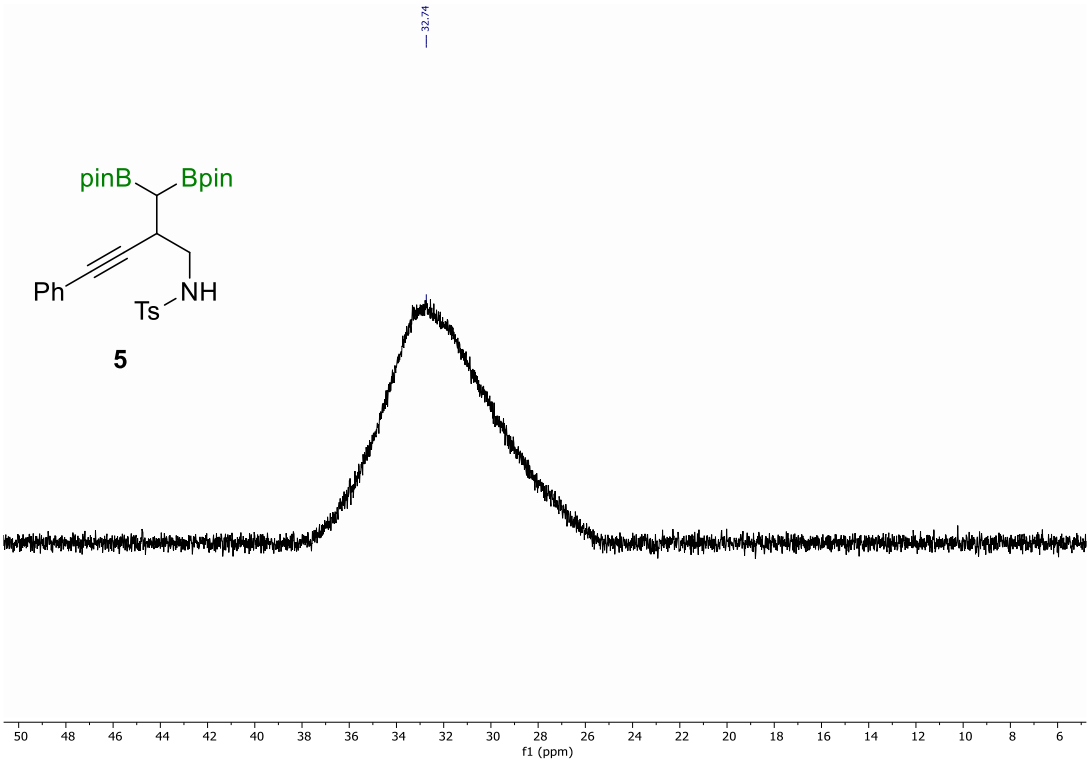
COSY-H Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (5)



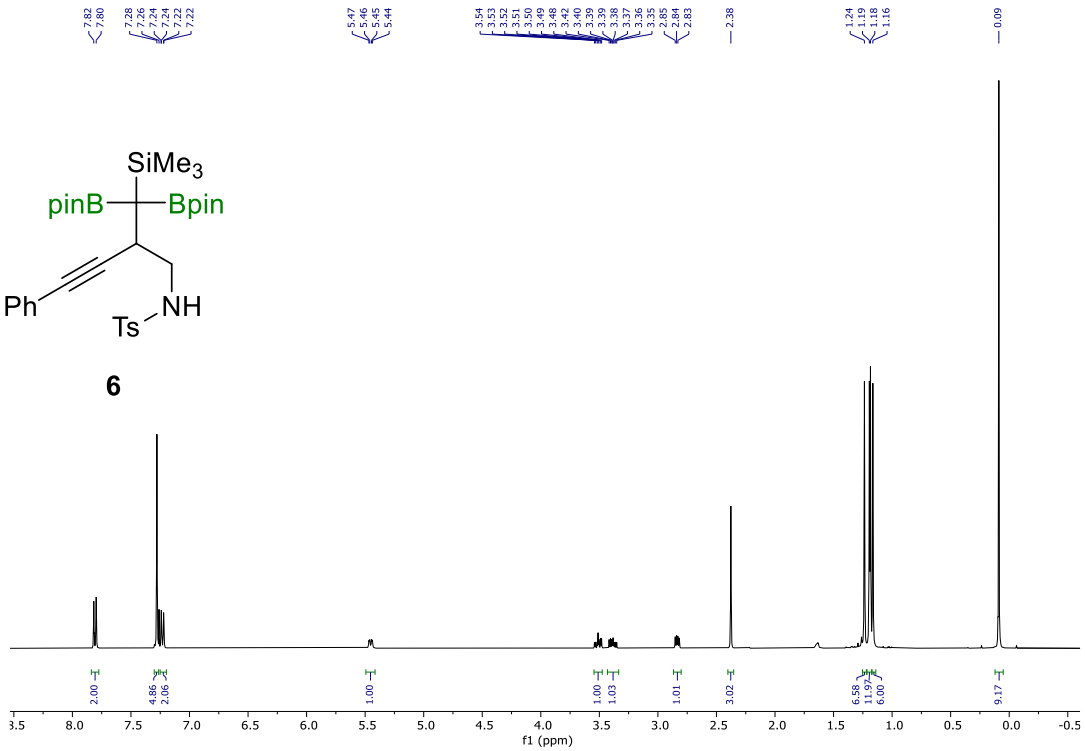
^{13}C NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (5)



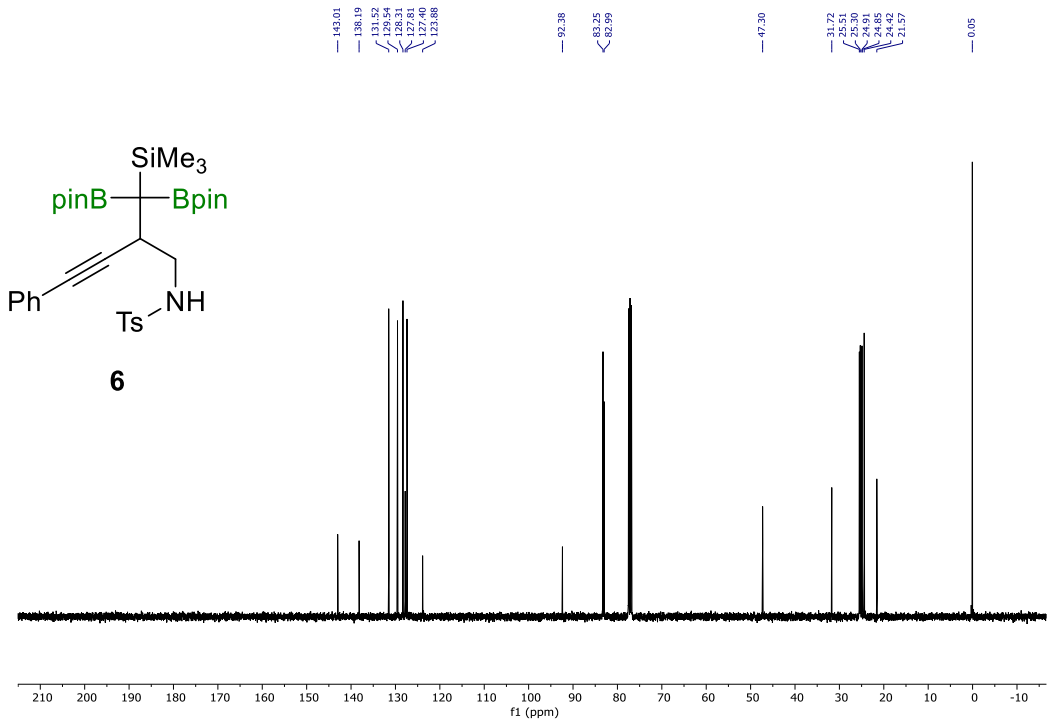
^{11}B NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (5)



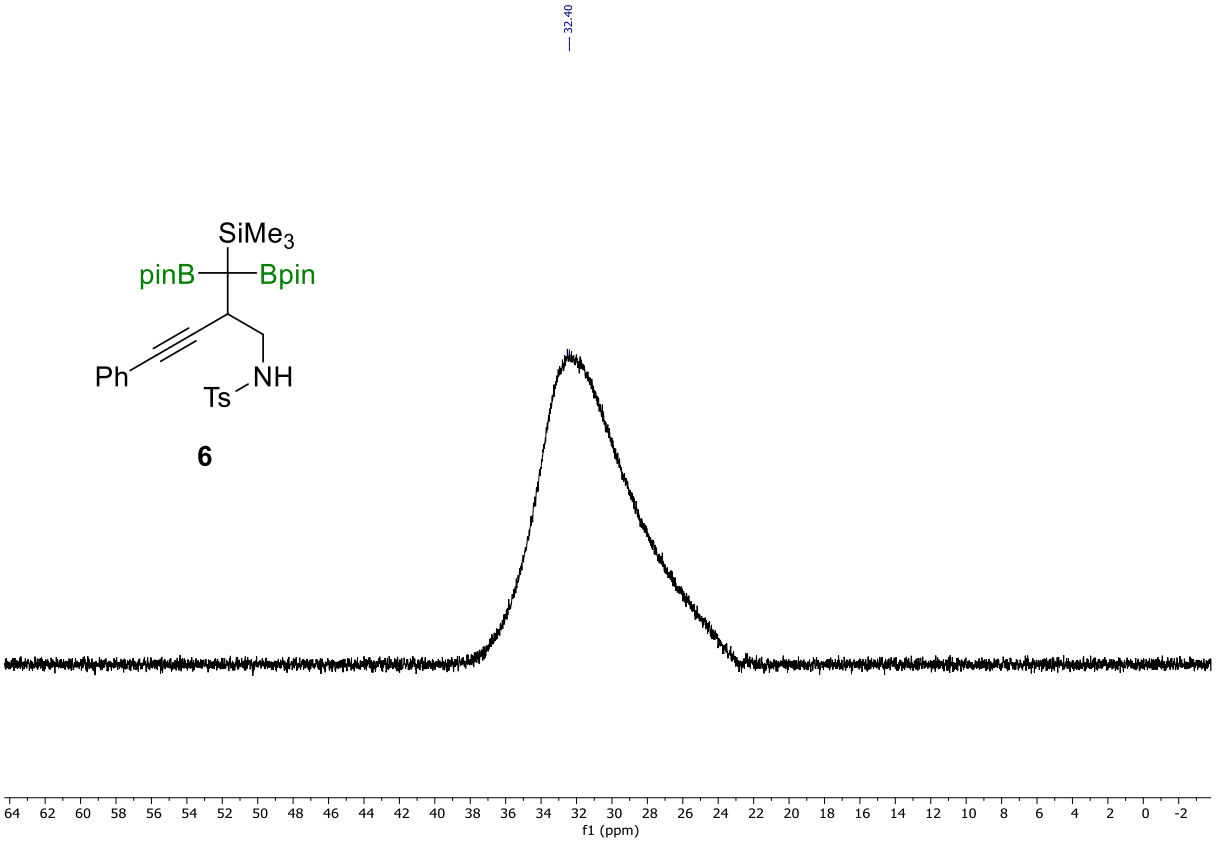
^{1}H NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (6)



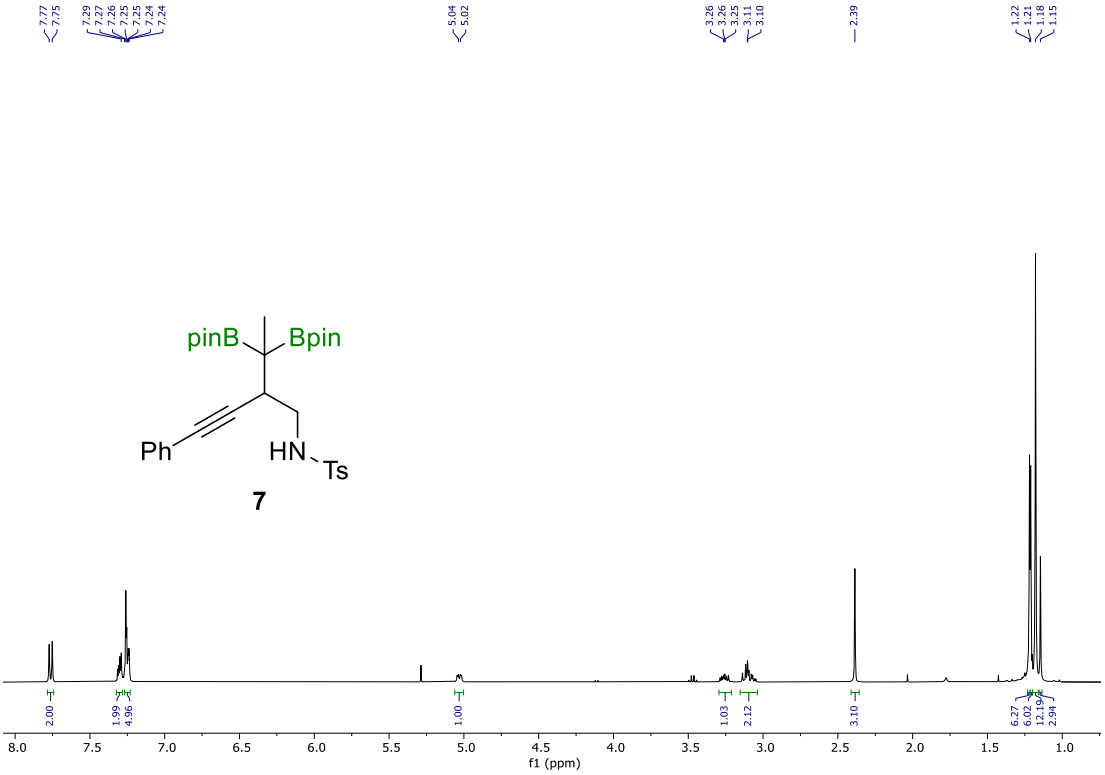
^{13}C NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (6)



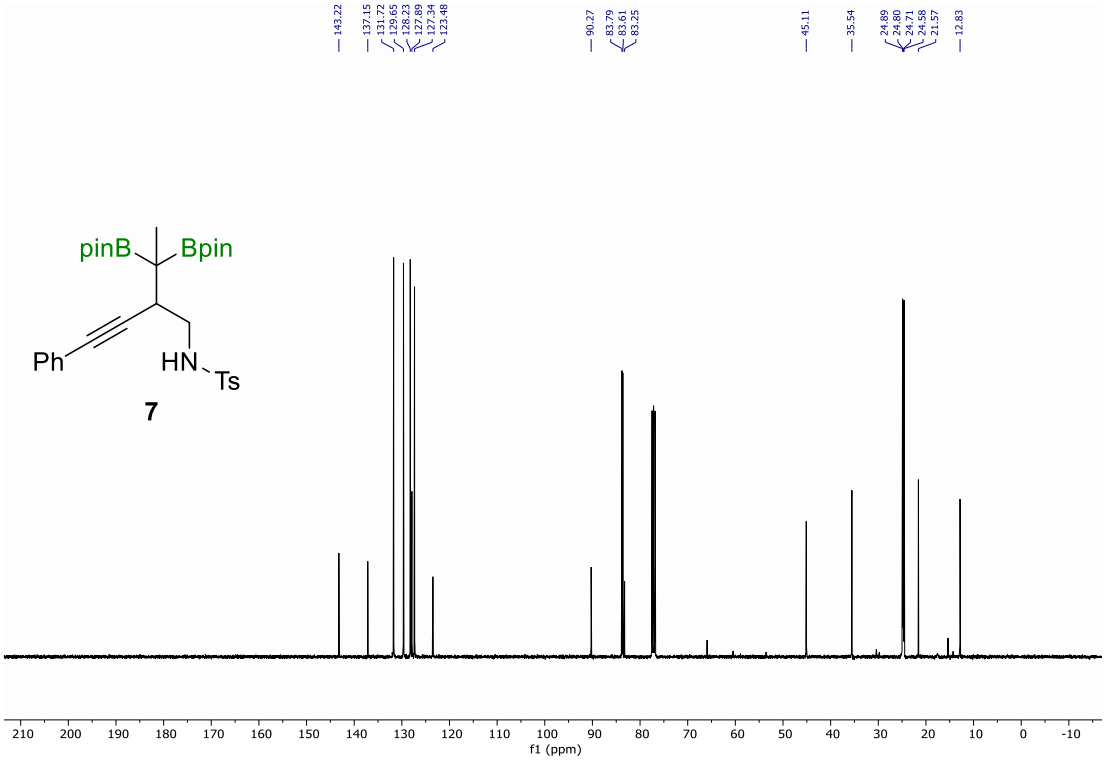
^{11}B NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (6)



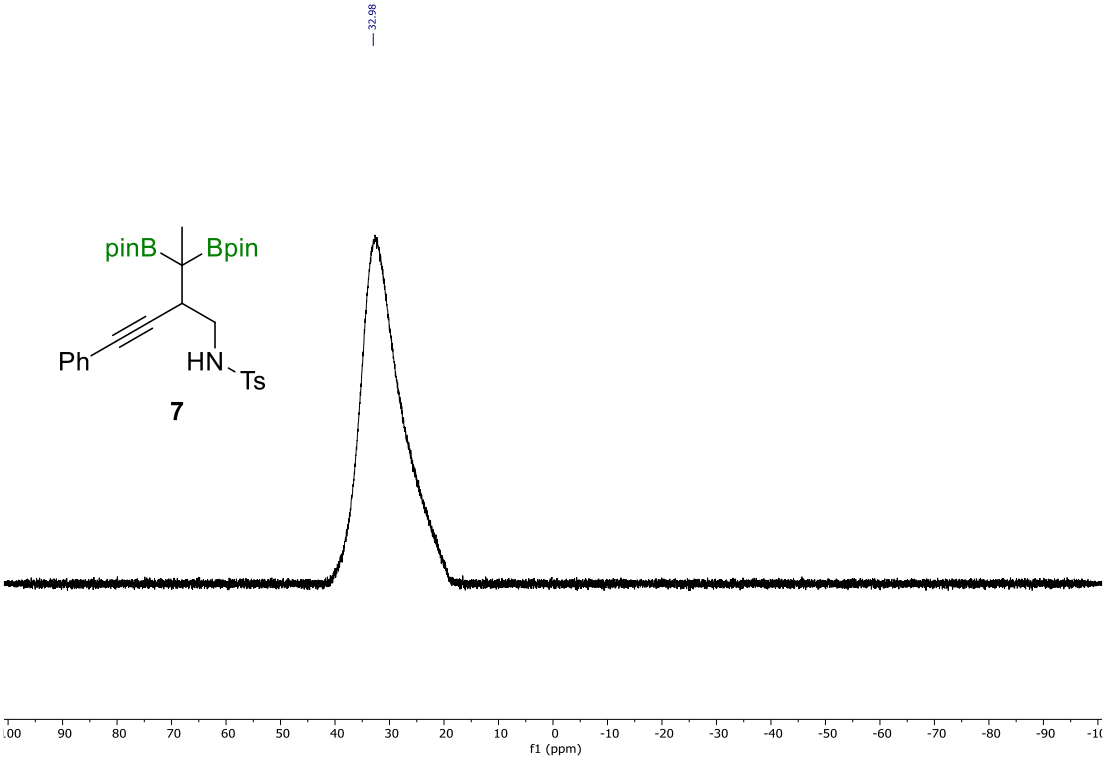
^{1}H NMR Spectrum of N-(2-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (7)



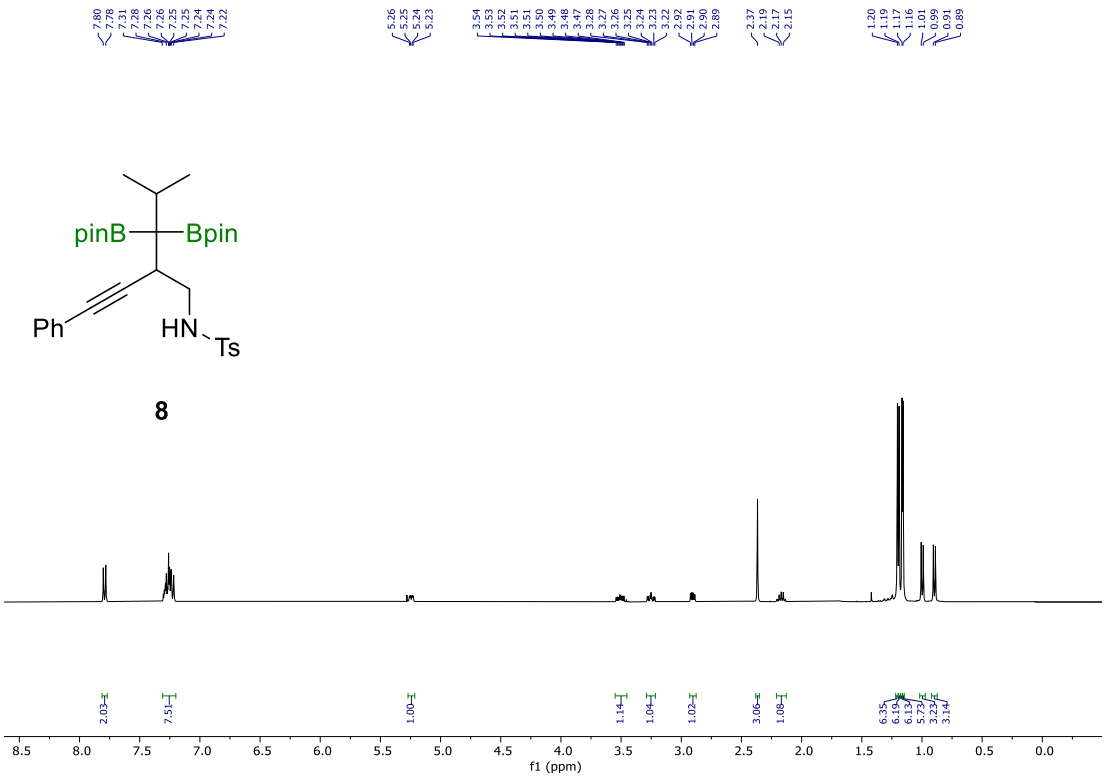
^{13}C NMR Spectrum of N-(2-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (7)



^{11}B NMR Spectrum of N-(2-(1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-4-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (7)



^{1}H NMR Spectrum of 4-Methyl-N-(4-methyl-2-(phenylethynyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzenesulfonamide (8)



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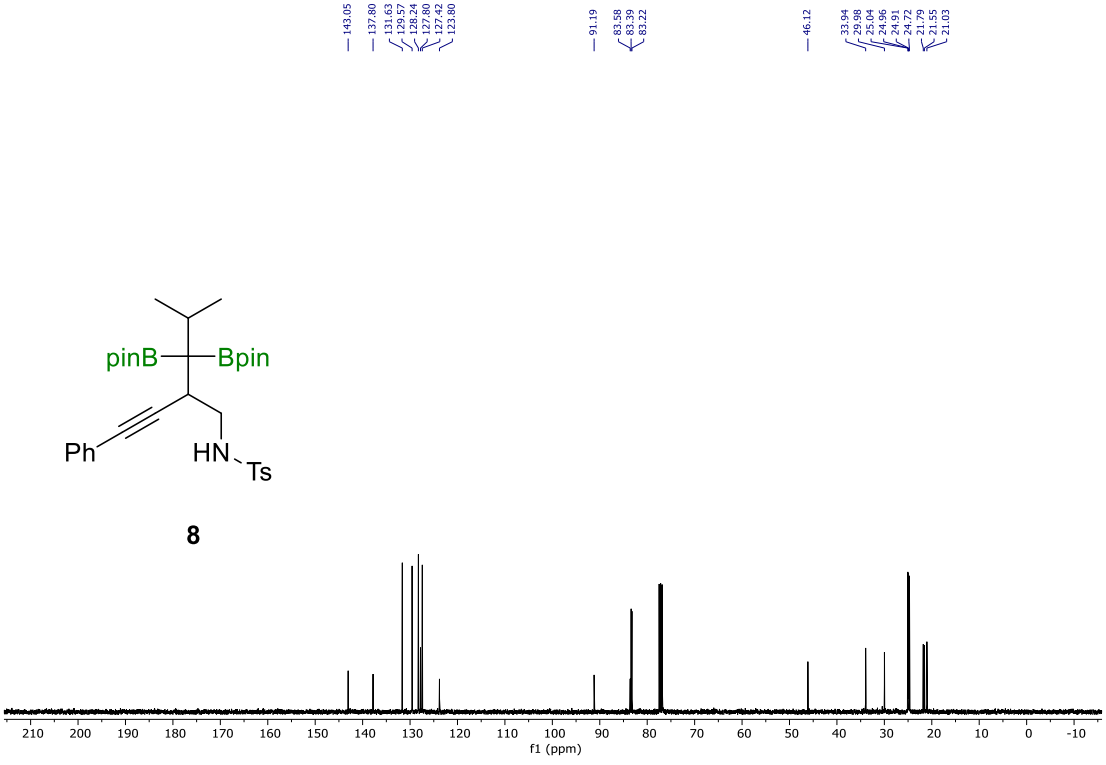
^{13}C NMR Spectrum of 4-Methyl-N-(4-methyl-2-(phenylethynyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzenesulfonamide (8)



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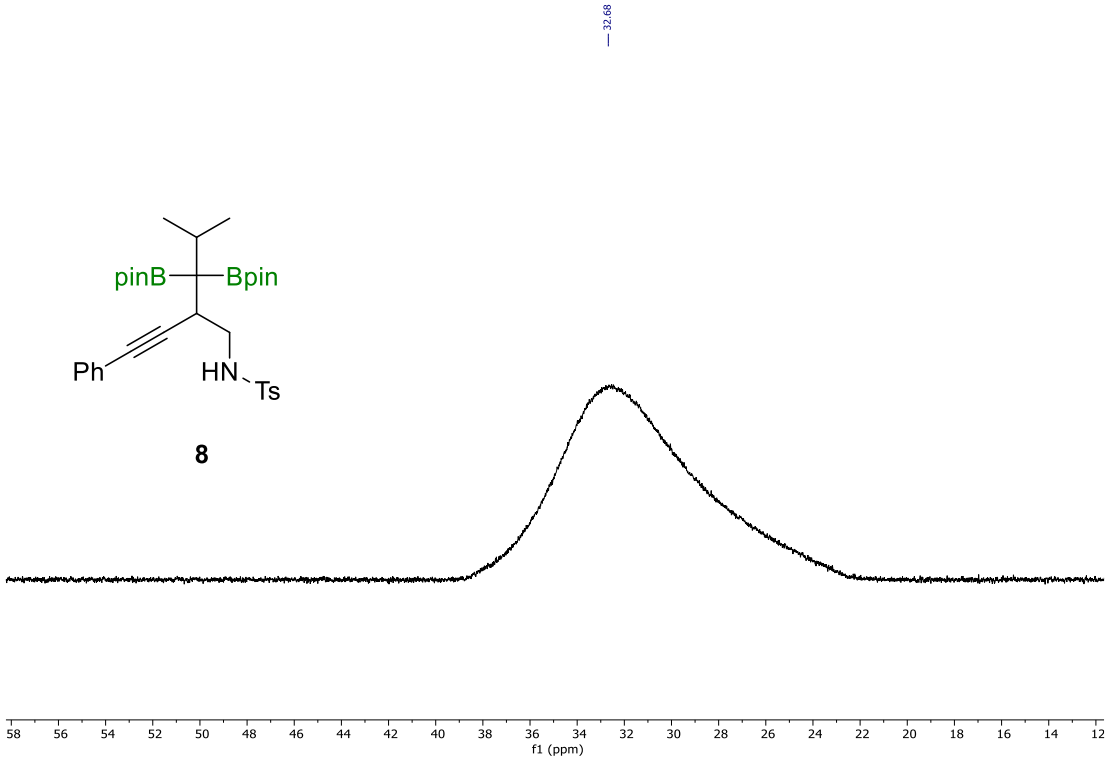
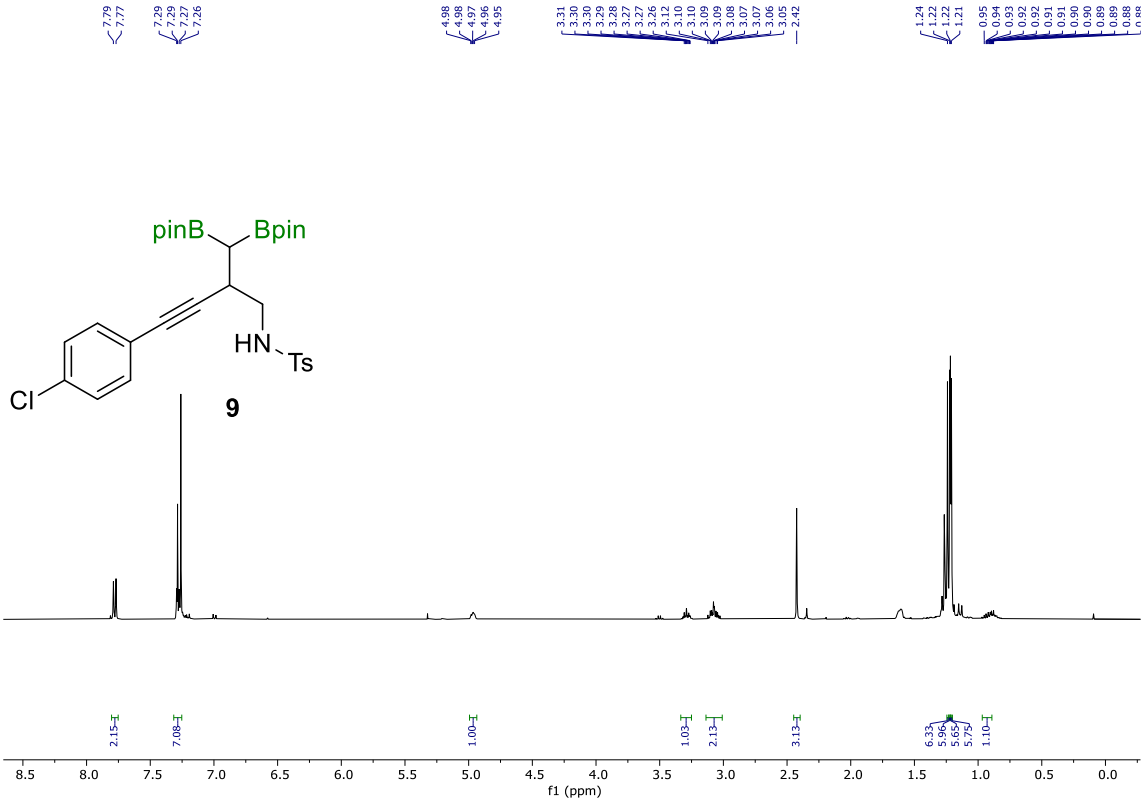
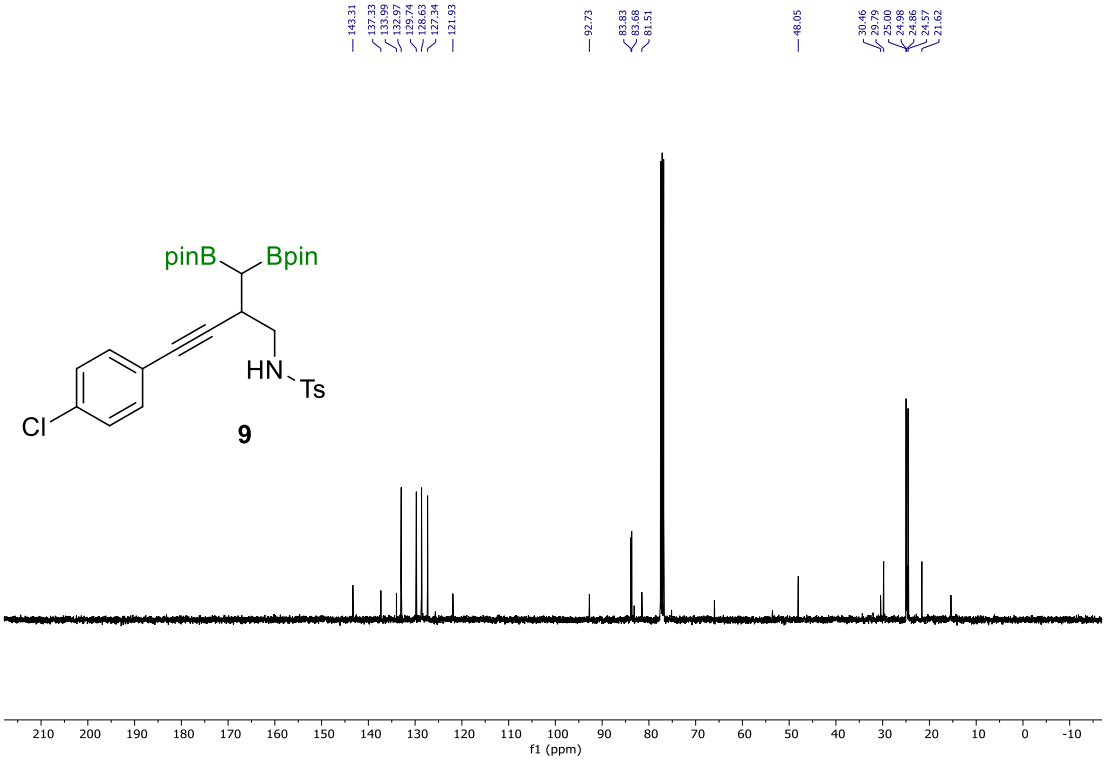
^{11}B NMR Spectrum of 4-Methyl-N-(4-methyl-2-(phenylethynyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)benzenesulfonamide (8)



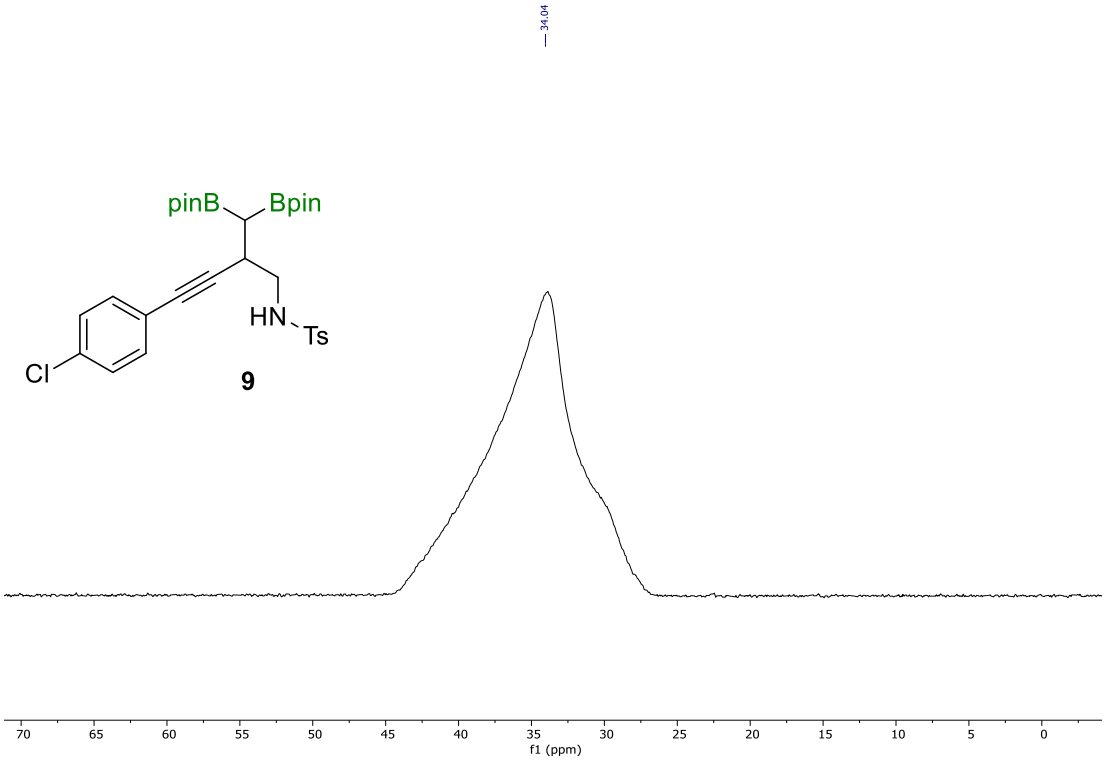
^{1}H NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (9)



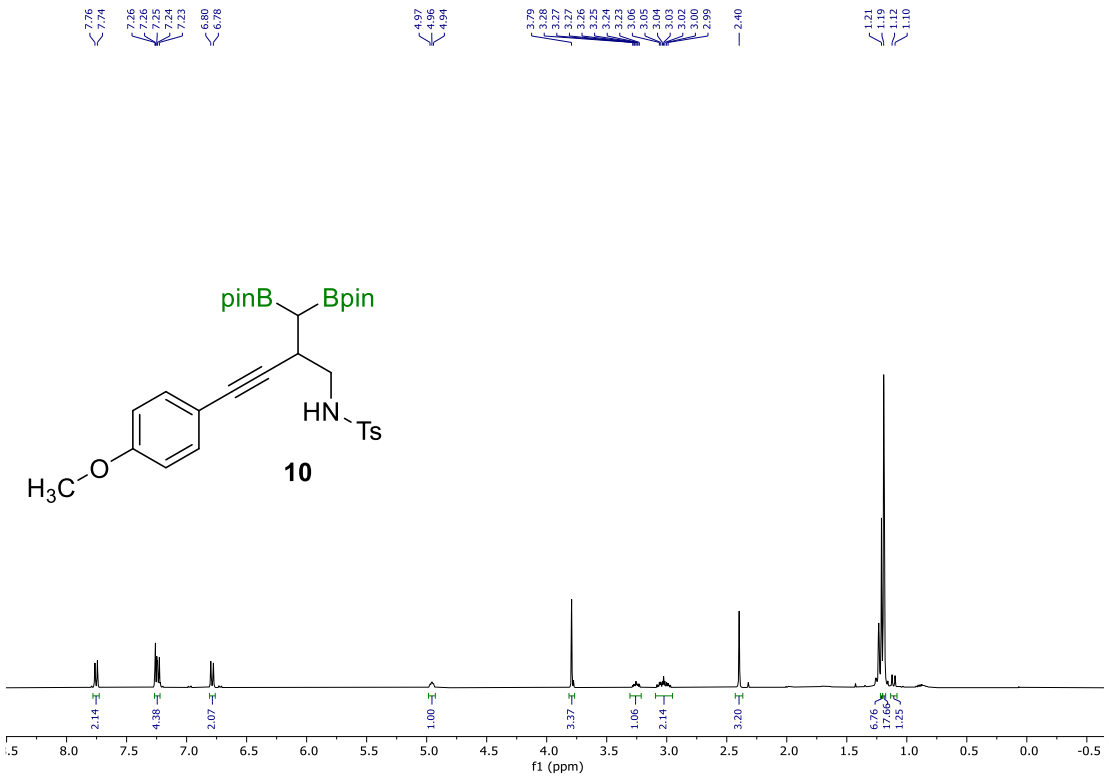
^{13}C NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (9)



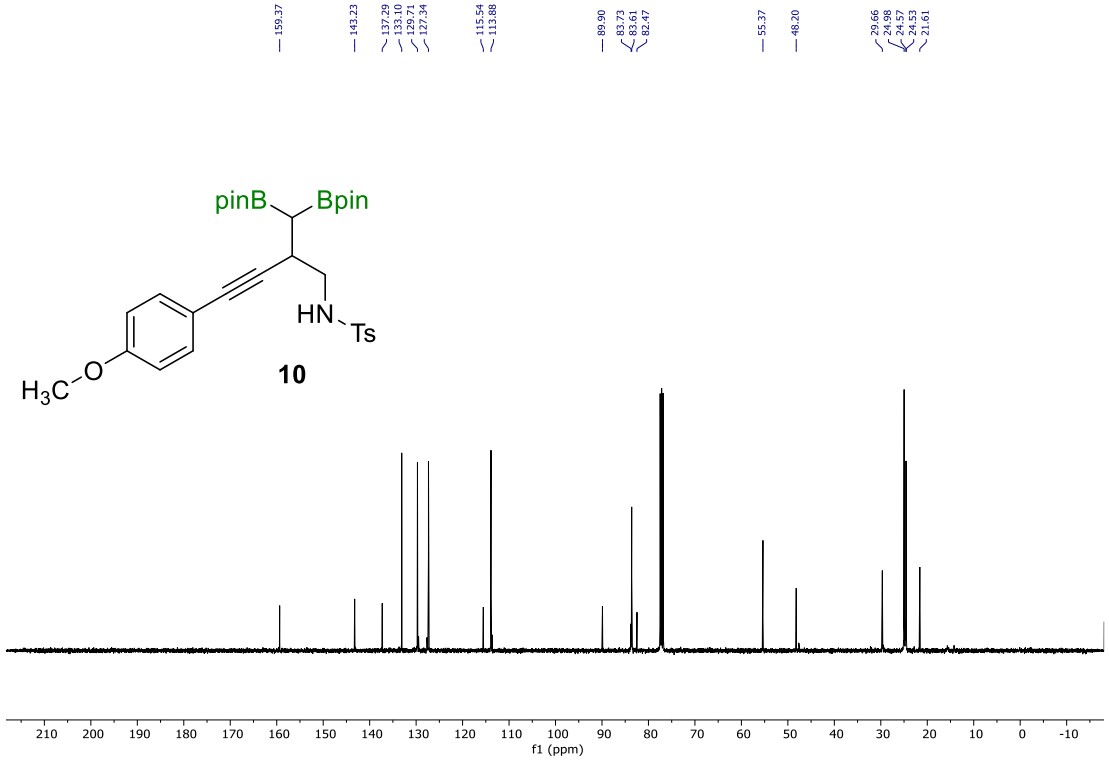
^{11}B NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-chlorophenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (9)



^{1}H NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (10)



^{13}C NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (10)



^{11}B NMR Spectrum of N-(2-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (10)