



## THESIS / THÈSE

### MASTER IN CHEMISTRY RESEARCH FOCUS

#### Triptycenes as platform for the design of new bulky boron lewis acids

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**Université de Namur**

**Faculté des Sciences**

**TRIPTYCENES AS PLATFORM FOR THE DESIGN OF NEW  
BULKY BORON LEWIS ACIDS**

**Mémoire présenté pour l'obtention  
du grade académique de Master Chimie «Chimie du Vivant et des Nanomatériaux» : Finalité Approfondie**

Xavier ANTOGNINI SILVA

Janvier 2019

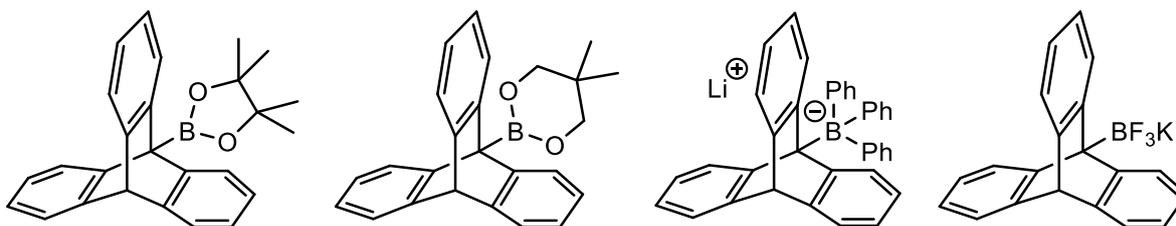
## Conception de nouveaux acides de Lewis borés dérivés du triptycène

ANTOIGNINI SILVA Xavier

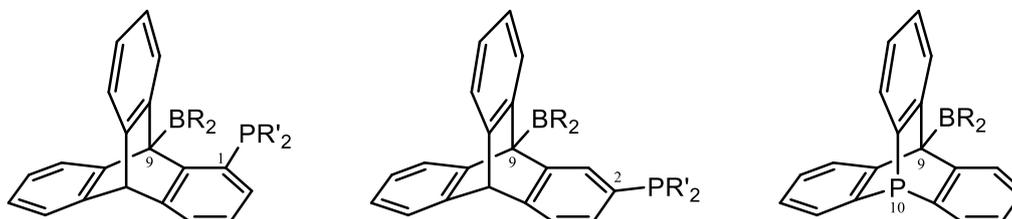
### Résumé

Grâce à leurs propriétés chimiques, physiques et photophysiques particulière les composés organiques borés jouent un rôle important en chimie des matériaux et en chimie organique. Les acides de Lewis borés stériquement encombrés sont de plus en plus utilisés en catalyse, en particulier dans le domaine des paires de Lewis frustrées.

Nous avons donc focalisé notre travail sur la conception d'acides de Lewis borés possédant un substituant triptycène, lié en tête de pont. Différentes méthodologies pour fonctionnaliser la position 9 du triptycène par un atome de bore ont été explorées. Cela a pu mener à la conception de différents composés borés pouvant servir de précurseurs d'acides de Lewis encombrés, voire de catalyseurs bifonctionnels.



En effet, le triptycène, possédant un grand nombre de positions fonctionnalisables, est un composé aromatique tridimensionnel très intéressant. Il est envisageable d'avoir, en plus du groupement boré en tête de pont, un groupement phosphoré à une autre position. Ces composés pourraient être utilisés en tant que catalyseurs bifonctionnels dans le domaine de paires de Lewis frustrées pour l'activation de petites molécules, telles que H<sub>2</sub>, CO<sub>2</sub> or CH<sub>4</sub>.



*Je tiens à remercier le professeur Guillaume Berionni de m'avoir permis de rejoindre son laboratoire RCO en tant qu'étudiant pour la réalisation de mon mémoire. Je le remercie pour sa constante motivation à se montrer disponible pour la bonne réalisation de ce projet et pour le temps qu'il a pris pour discuter des différents aspects qu'un tel travail implique.*

*Je souhaite également remercier particulièrement Aurélien Chardon, pour les nombreux conseils pratiques qu'il a donné pour la bonne réalisation des manipulations ainsi que pour le partage de sa grande connaissance dans beaucoup de domaines de la chimie organique, et plus particulièrement dans le domaine de la chimie du bore.*

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*Finalement, je tiens à remercier profondément ma famille, et plus particulièrement mes parents qui m'ont apporté de la motivation et de la confiance tout au long de mon cursus et qui ont été derrière moi en toutes circonstances.*

*Xavier*

## Abbreviations et symboles :

Å	angström	min	minute
Ac	acetyl	mL	millilitre
Am	amyl	mmol	millimole
Bu	butyl	mol	mole
<i>n</i> -Bu	<i>n</i> -butyl	NMR	nuclear magnetic resonance
<i>t</i> -Bu	<i>tert</i> -butyl	neo	neopentyl glycolato
°C	Celsius degree	on.	overnight
CH <sub>2</sub> Cl <sub>2</sub>	dichloromethane	Ph	phenyl
Cp	cyclopentadienyl	pin	pinacolato
δ	chemical shift	<i>i</i> -Pr	isopropyl
ee	enantiomeric excess	<i>i</i> -PrOBpin	isopropylboronic acid pinacol ester
Et	ethyl	r.t.	room temperature
EtCN	ethyl cyanide	TBAF	tetra- <i>n</i> -butyl-ammoniumfluoride
Et <sub>2</sub> O	diethyl ether	THF	tetrahydrofuran
eq	equivalent	TMS	trimethylsilyl
FLP	frustrated Lewis pair	Tp	trityphenyl
g	gram	TpBpin	(9-trityphenyl)boronic acid pinacol ester
h	hour	Ts	tosyl
M	molar	vol	volume
Me	methyl		
MeOH	methanol		
Mes	mesityl		
mg	milligram		
MHz	megahertz		

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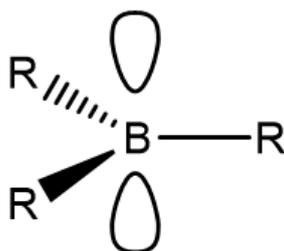
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# **1. INTRODUCTION**

## 1.1. Boron Lewis Acids

### 1.1.1. Generalities

In 1923, Gilbert N. Lewis stated that an acid substance can accept a pair of electrons in order to form a chemical bond.<sup>[1]</sup> With an electronegativity of 2.04 on Pauling scale<sup>[2]</sup> and with a vacant p-orbital (*Figure 1*), the boron atom in its trigonal  $sp^2$  hybridized form make trisubstituted organoboron derivatives very good Lewis acids.<sup>[3]</sup>

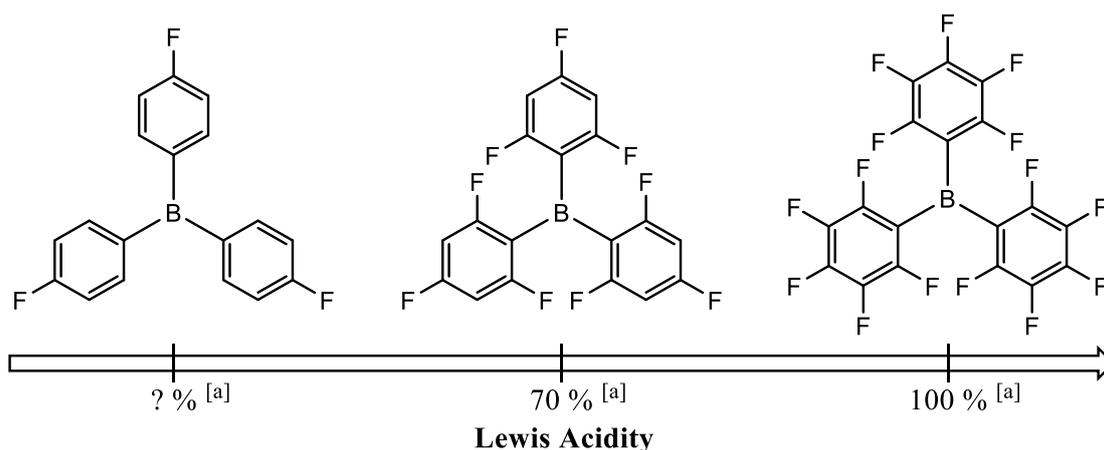


*Figure 1* - Vacant p-orbital in trigonal  $sp^2$  hybridized organoboron derivatives.

### 1.1.2. Factors influencing the Lewis acidity of trivalent boron compounds

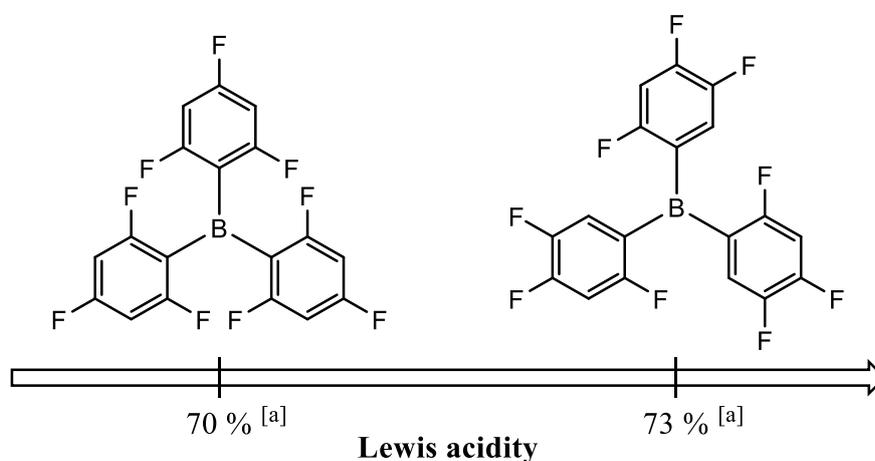
As a general rule, the Lewis acidity of trivalent boron compounds depends of the electronic nature of the substituents and of the geometry around the boron atom. Strongly electronegative atoms or electron withdrawing substituents will decrease the electron density around the boron atom therefore increasing its acidity. For substituents possessing a lone pair, the size of the p-orbital must be considered. Indeed, a strong overlap between the boron and the substituent p-orbitals will increase the charge donation from the lone pair of the substituent and then increase the electron density around the boron atom. This trend is well seen in the case of the boron trihalides in which the acidity decrease with the electronegativity of the halide ( $BI_3 > BBr_3 > BCl_3 > BF_3$ )<sup>[4]</sup> due to the fact that the considered overlap is stronger when the size of the halide decreases.

In the case of triarylboranes, an increasing number of electron-withdrawing groups on the aromatic rings will increase the boron electron deficiency proportionally to the strength of their electron-withdrawing strengths (*Figure 2*). The position of the substituents is also crucial since *ortho*-substituents will shield sterically the boron atom and will apparently decrease its acidity with respect to large Lewis bases. For example, mono-*ortho*-fluorinated boranes show a stronger acidity than the di-*ortho*-fluorinated ones for a same number of fluorine substituents (*Figure 3*).<sup>[5]</sup>



**Figure 2** – Lewis acidity of triarylboranes according to the number of electron-withdrawing group.

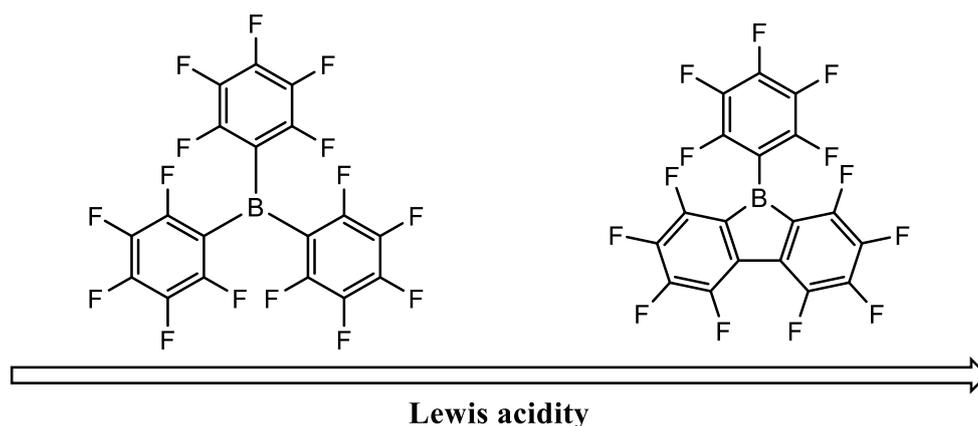
<sup>[a]</sup> Relative acidities calculated from Child's scale<sup>[5]</sup> (see section 1.1.3)



**Figure 3** – Increasing Lewis acidity for mono-ortho-fluorinated triarylborane in respect to the di-ortho-fluorinated one with the same number of fluorine.

<sup>[a]</sup> Relative acidities calculated from Child's scale<sup>[5]</sup>

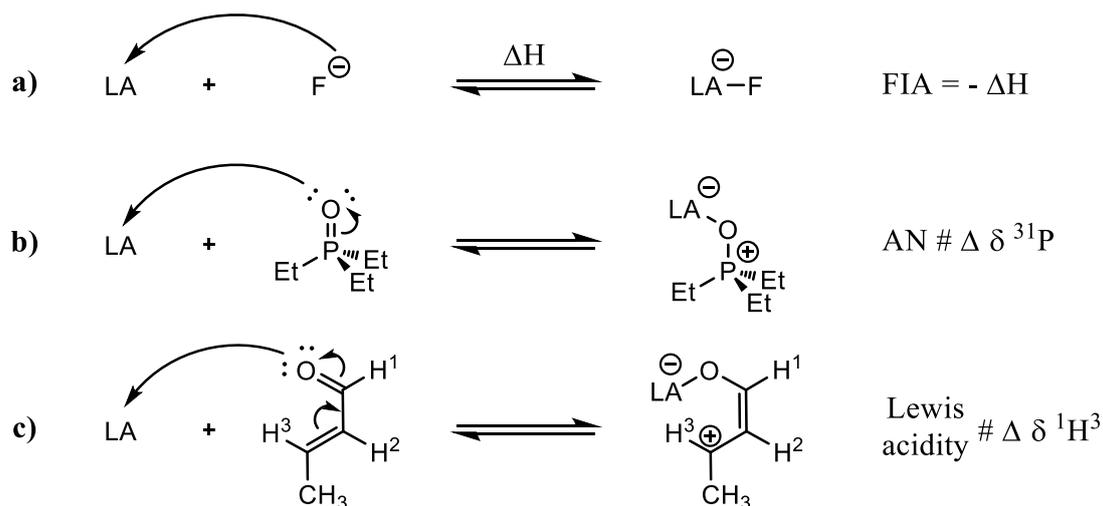
Another factor is the geometry of the triarylboranes. Indeed, as stated earlier, a higher steric accessibility of the boron center will increase the acidity due to the fact that it will be more able to coordinate with the Lewis base. For planar boranes incorporating the boron atom into a rigid planar framework, the strain from electronic repulsions of the substituents that is encountered during the pyramidalization of the boron centre that occurs upon complexation of the Lewis base will be lowered. For example, the acidity will be enhanced when we go from tris(pentafluorophenyl)borane to perfluorinated 9-boraphenylfluorene (**Figure 4**).<sup>[6,7]</sup>



**Figure 4** – Increase of Lewis acidity by incorporating the boron atom into a planar framework.

### 1.1.3. Lewis acidity scales

The strength of Lewis acids can not be arranged into a unique order that would be applicable for all reactions with Lewis bases. Indeed, as stated by Mulliken in 1952, the strength of a Lewis acid is not an absolute quantity but depends on specific features of its interaction with the Lewis base it is paired with.<sup>[8]</sup> Therefore, different Lewis acidity scales are currently used and were constructed by determining the interaction of several Lewis acid with a selected reference Lewis base. For example the fluoride ion affinity (FIA) is a widely used scale based on theoretical or experimental calculation of the enthalpy of association of the Lewis acid with the fluoride ion  $F^-$  (**Figure 5a**).<sup>[9]</sup> This strong Lewis base is chosen as a reference because it reacts quantitatively and rapidly with almost all Lewis acid owing to its small size, high basicity and high electronegativity. Another way to rank the Lewis acids is the Gutmann-Beckett method. The strength of the Lewis acid is described by a parameter called AN (Acceptor Number), calculated from the  $^{31}P$  NMR shift of triethylphosphine oxide after complexation, leading to a deshielding of the phosphorous atom (**Figure 5b**).<sup>[10]</sup> The strongest the Lewis acid is, the most the electron density around phosphorous will decrease, the higher will be its chemical shift. Another scale based on NMR spectroscopy is obtained by the Child's method. The strength of the Lewis acid is described by the  $^1H$  NMR chemical shift variation of the  $H_3$  proton of crotonaldehyde upon complexation of both compounds (**Figure 5c**).<sup>[11]</sup> Here again, the chemical shift will increase downfield with the strength of the Lewis acid.

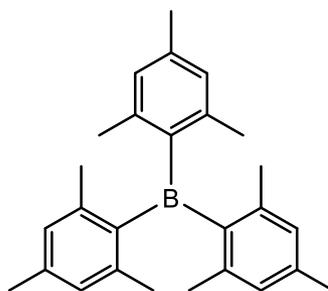


*Figure 5 – Considered reactions and parameters for the different Lewis acidity scales.*

#### 1.1.4. Steric hindrance

The steric hindrance is a steric effect in which the spatial organisation of the atoms or groups in a molecule around the reactive site partially or totally inhibits a chemical process (reaction, bond formation, association...). Indeed, for a reaction between two molecules to be achieved, each reactive centre must be able to get close enough (at least the size of the sum of the Van der Waals radii of the two considered atoms) to allow the formation of a covalent bond.<sup>[12]</sup>

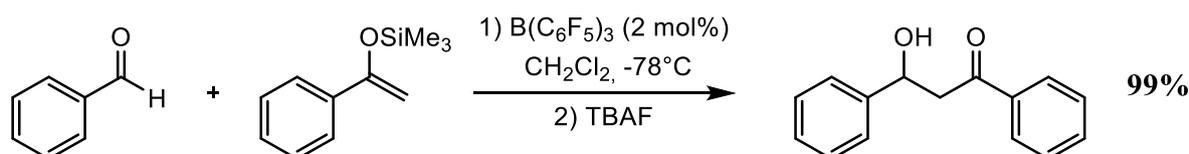
The steric hindrance is a very interesting factor in boron chemistry since the sterically hindered boron compounds show very different properties than their non-hindered analogues.<sup>[13]</sup> Indeed, the change in reactivity of triarylboranes depending on the size of its substituents is due to the fact that reactions of such compounds usually involve an attack on the boron-carbon bond which is less likely to happen when the boron atom is shielded by surrounding large aryl groups.<sup>[14]</sup> For example, while non-hindered boron compounds are highly sensitive to reactions involving the boron-carbon bond cleavage (i.e. protodeborylation), trimesitylborane (**Figure 6**) is very unreactive to water and to oxygen and also shows no reactivity toward bases such as ammonia or triethylamine.<sup>[15]</sup>



**Figure 6** – Structure of trimesitylborane.

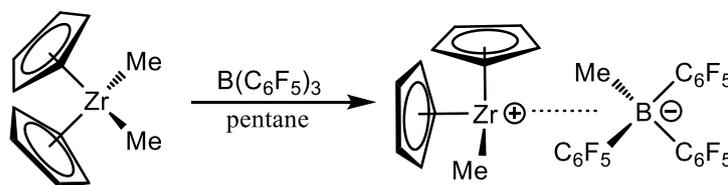
### 1.1.5. Applications of triarylboranes

Boron Lewis acids are used as catalysts in organic chemistry and as activators for organometallic catalysis. In recent years, the tris(pentafluorophenyl)borane  $B(C_6F_5)_3$  has been increasingly used as catalyst to perform conjugate addition of silyl enol ethers or ketene silyl acetals such as Mukaiyama aldol reactions type (**Figure 7**), Sakurai-Hosomi allylation, hydrosilylation of aromatic aldehydes, ketones and esters, ...<sup>[16]</sup>



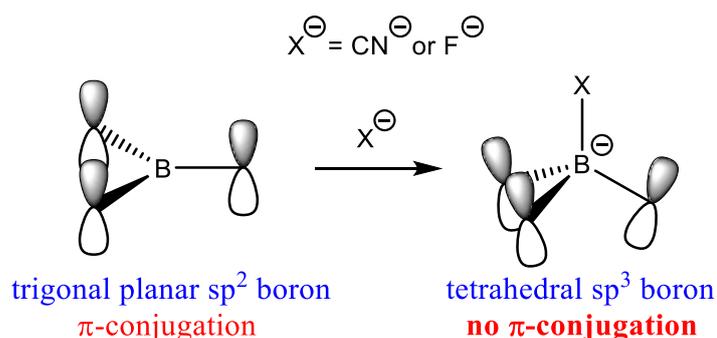
**Figure 7** – Example of aldol-type reaction catalysed by tris(pentafluorophenyl)borane.<sup>[17]</sup>

$B(C_6F_5)_3$  is also used for the catalysis of homogeneous olefin polymerisation. Indeed, this powerful Lewis acid is able to abstract a methyl group from a metal centre leading to the creation of a cationic organometallic species (**Figure 8**) which has the required reactivity for olefin chain reaction.<sup>[18]</sup>



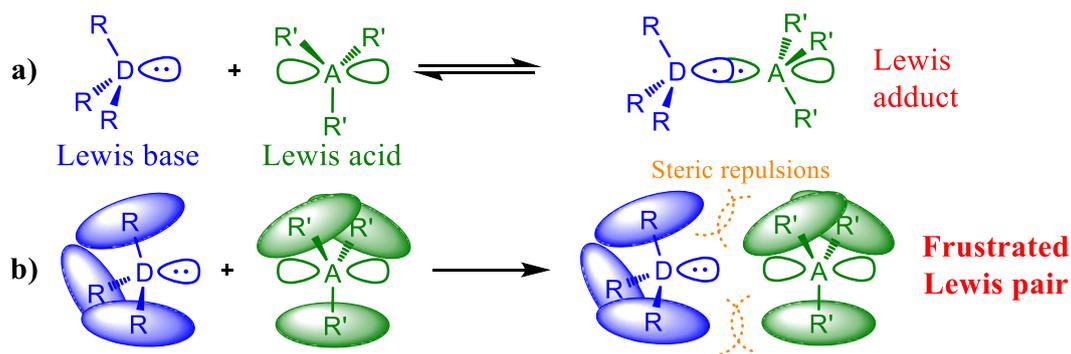
**Figure 8** – Methyl abstraction from dimethylzirconocene by tris(pentafluorophenyl)borane.

Triarylboranes are also used for the detection of anions and especially fluoride anion thanks to the strong affinity of boron atom toward the fluoride anion.<sup>[19]</sup> The detection can be readily monitored by spectrophotometric methods since the binding of the anion to the boron atom induces a property change, such as a color change. Indeed, the  $\pi$ -electron system of boron-based anion sensors is interrupted due to a geometry change when the fluorine anion binds to the boron atom (**Figure 9**).<sup>[20]</sup>



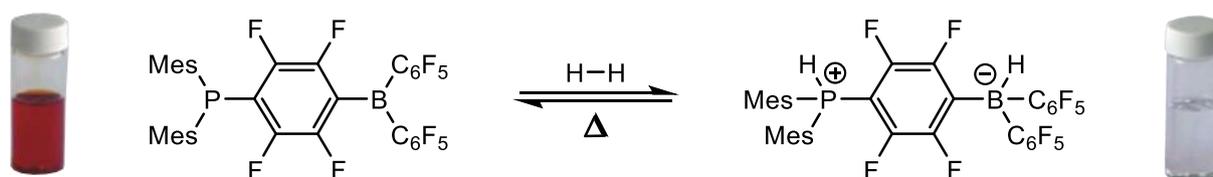
**Figure 9** – Schematic representation of the interruption of  $\pi$ -conjugation induced by the binding of an anion to the boron atom.

Triarylboranes are amongst the most popular constituents of frustrated Lewis pairs (FLP) for the activation of small molecules in combination with Lewis bases. Usually, when a Lewis acid and a Lewis base interact together they form a so-called Lewis adduct (**Figure 10a**). But when both systems are sterically hindered, they are not able to form the Lewis adduct due to the steric repulsions and they make a system called a frustrated Lewis pair (**Figure 10b**). In such a system, both constituents can act as Lewis acid and base on other small molecules.<sup>[21]</sup>



**Figure 10** – a) Formation of a Lewis adduct with non-hindered Lewis base and Lewis acid and b) formation of a frustrated Lewis pair with hindered Lewis base and Lewis acid.

The very first non-transition metal system that was able to reversibly take up and release dihydrogen was an intramolecular FLP developed by Douglas Stephan in 2006 (**Figure 11**).<sup>[22]</sup> For intermolecular FLPs, most of the Lewis bases and acids used are phosphines and boranes. The requirements for the activation of H<sub>2</sub> include both a sterically hindered system and a favourable combination with a threshold limit in Lewis acidity and basicity. For these reasons, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is the mostly used Lewis acid in this field in combination with hindered phosphines.<sup>[21]</sup>

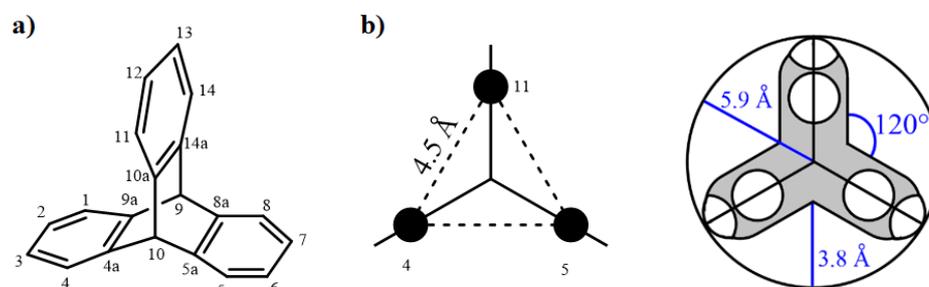


**Figure 11** – First non-transition metal system able to reversibly take up and release dihydrogen.

## 1.2. Triptycene

### 1.2.1. Generalities

Triptycene belongs to the ipitycene family and is constituted of three aromatic rings connected together with a bicyclo[2.2.2]octane framework (**Figure 12**).<sup>[23]</sup> These three arene units are maintained by this rigid scaffold with an angle of 120° between each aromatic rings which allows a wide free volume between them.<sup>[24]</sup>

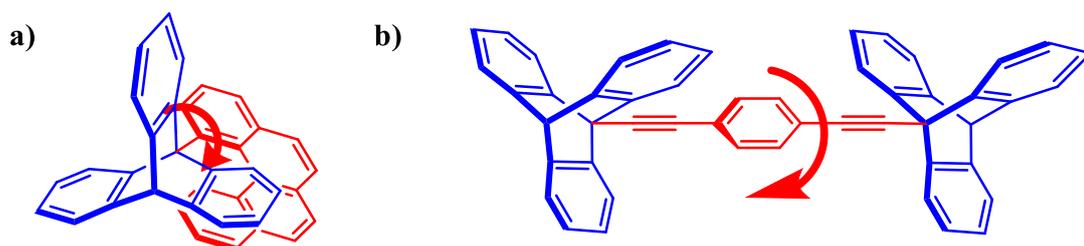


**Figure 12** - a) Structure, nomenclature and b) geometrical properties of triptycene.<sup>[24,25]</sup>

The particular structure and properties of triptycene derivatives make them interesting for many applications in chemistry.<sup>[23]</sup> For example, they are used to design molecular machines, molecular balances, rigid complexes in catalysis, hosts in supramolecular chemistry, three-dimensional platform for materials chemistry or crystal engineering as described below.<sup>[26]</sup>

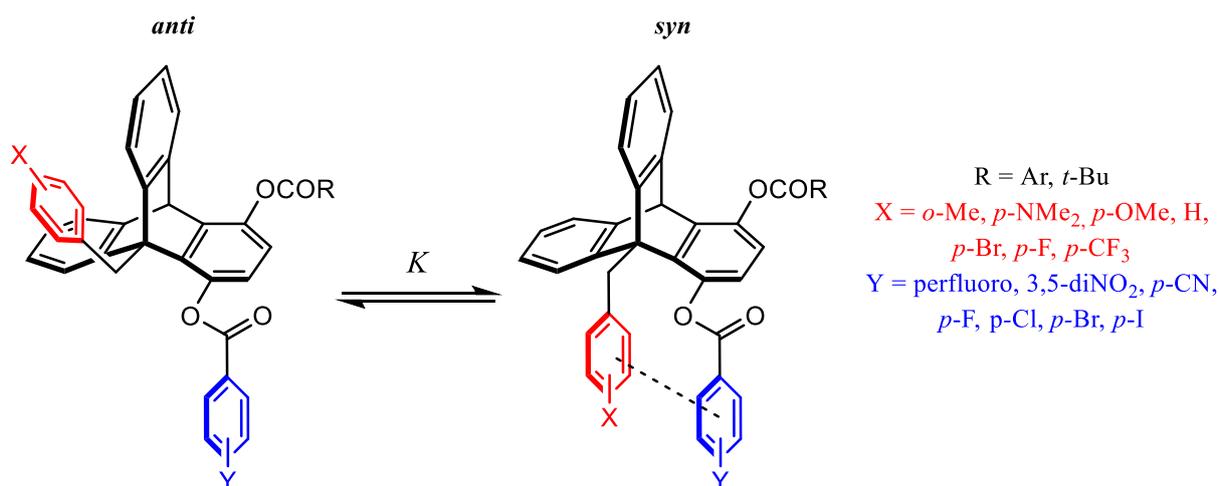
## 1.2.2. Applications

The triptycene can be used to design molecular machines. Those are interchangeable molecular systems able to produce a mechanical work from energy which can come from electronic or nuclear rearrangements or from a stimuli generating a Brownian motion.<sup>[27]</sup> Examples of molecular gyroscope with the triptycene scaffold has been established by the group of Kelly in 1999<sup>[28]</sup> (**Figure 13a**) and the group Garcia-Garibay in 2002<sup>[29]</sup> (**Figure 13b**). The rotation is involved respectively by thermal stimulation and by the response of the polarizable aromatic ring to an external field.



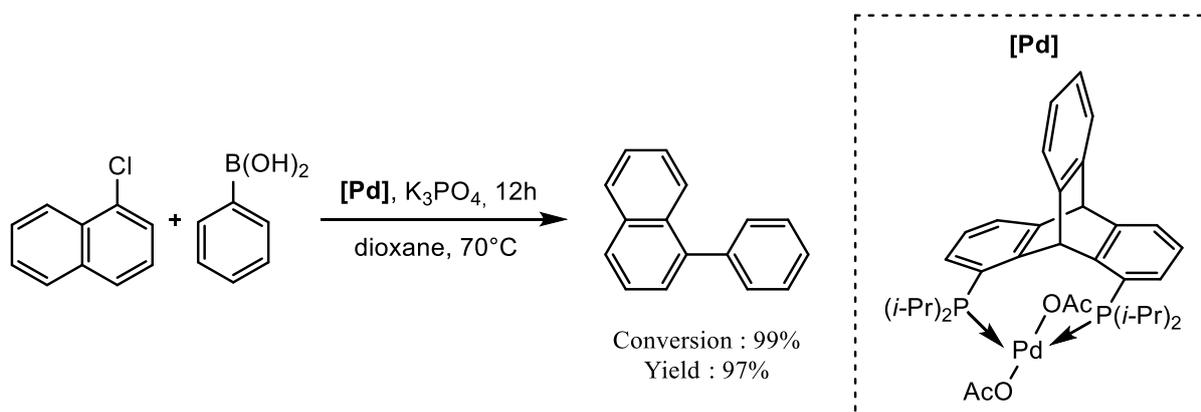
**Figure 13** – Molecular machines with a triptycene scaffold established by the group of a) Kelly<sup>[28]</sup> and b) Garcia-Garibay<sup>[29]</sup>.

Triptycene can also be used for the design of molecular balances. Those are systems able to quantify molecular interactions thanks to the determination of the relative stabilities of conformational states.<sup>[30]</sup> Examples of molecular balances with the triptycene scaffold for the quantification of offset aromatic stacking interactions have been established by the group of Gung in 2005<sup>[31]</sup> (**Figure 14**).



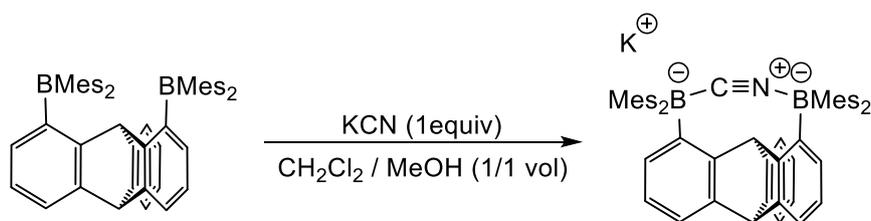
**Figure 14** – Molecular balances with a triptycene scaffold for the quantification of offset aromatic stacking established by the group of Gung in 2005.<sup>[31]</sup>

Triptycene scaffold can also be used for the design of rigid complexes in catalysis. The rigidity constraints of a ligand for the chelation of a metal lead to an enhanced affinity between both species by kinetic stabilisation of the complex.<sup>[32]</sup> An example of this kind of rigid complexes for the catalysis of C-C bond formation has been established by the group of Gelman in 2005<sup>[33]</sup> (**Figure 15**).



**Figure 15** – Formation of 1-phenylnaphthalene by C-C bond formation with a palladium complex with the triptycene scaffold.<sup>[33]</sup>

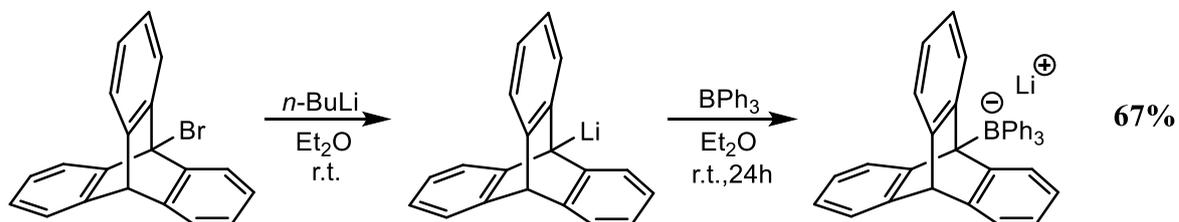
Only two examples of boron substituted triptycene have been described in the literature. For example, a diborane compound using triptycene scaffold as a linker has been reported by Gabbai in 2018<sup>[34]</sup> and was used for the detection of cyanide anions (**Figure 16**). The second example of boron-substituted triptycene is described in the next section.



**Figure 16** – Disubstituted triptycene with a boron atom for the detection of cyanide anions.

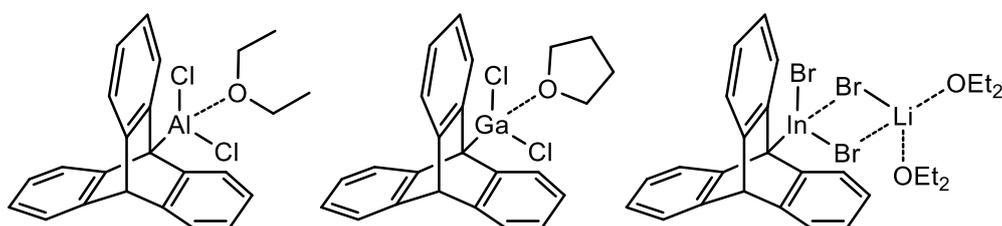
### 1.3. Triptycenes substituted in the 9-position

To the best of our knowledge, only a single example of 9-substituted boron triptycene has been reported in a landmark publication of Wittig in 1962<sup>[35]</sup> (**Figure 17**).



**Figure 17** - Wittig's synthesis of lithium (9-triptyceny)triphenylborate.

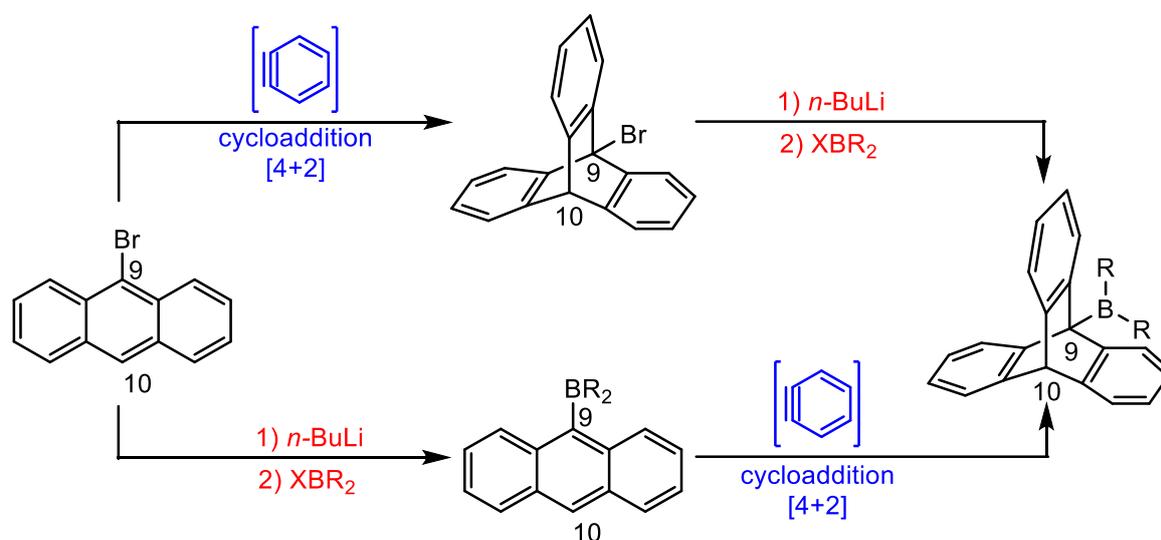
Surprisingly, not any other boron compounds derived from triptycene substituted in the 9-position has been reported up to date despite of all the potential of the triptycene platform. In addition, only one article describes group XIII elements triptycenes substituted at the 9-position with an aluminium, gallium or indium atom and surprisingly the boron substitution was not described (**Figure 18**).<sup>[36]</sup> These compounds have been synthesized in order to use the triptycene scaffold as a sterically demanding ligand that will stabilize the metal(I) diyls moiety.



**Figure 18** – Only known triptycenes complexes with a trivalent Lewis acidic atom at the 9-position.

## **2. OBJECTIVES**

Only very few triptycene-derived Lewis acids have been synthesized, and to the best of our knowledge there are not any applications in catalysis. The goal of our research is therefore to use the triptycene scaffold as a “very bulky substituent” to synthesize completely new types of highly hindered boron Lewis acids for potential applications in catalysis. The major part of this project was the study of the challenging insertion of a boron atom at the position 9 of triptycene (i.e. the bridgehead and the most hindered position). To this end, we mainly investigated two different pathways (*Figure 19*).

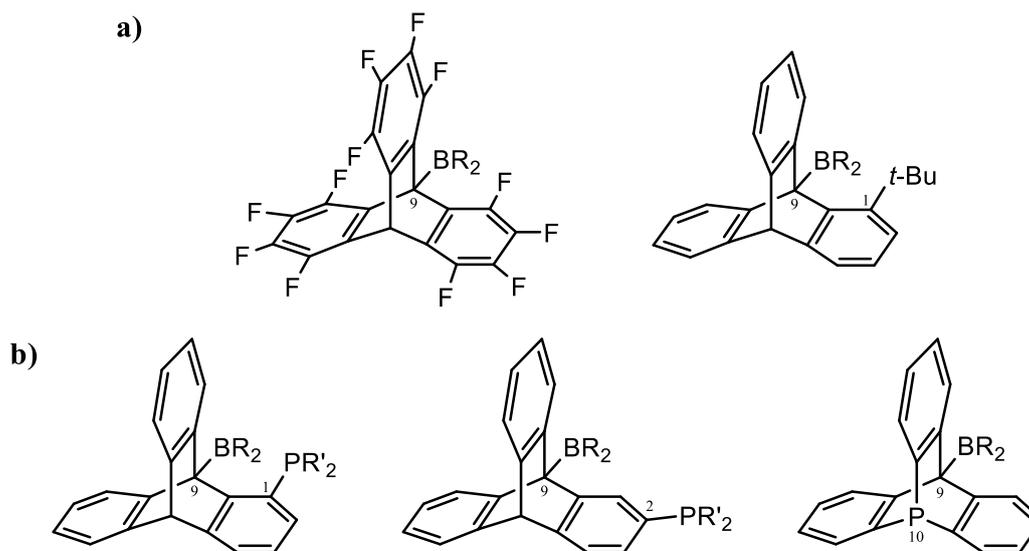


*Figure 19* – Synthetic pathways investigated for the obtention new types of highly hindered boron Lewis acids.

This led us to the synthesis of new boron compounds with a triptycene scaffold. As a second goal, we planned to investigate the structures of our boron-triptycenes by X-ray analysis and by theoretical calculations in order to rationalize their steric hindrance and to compare it with classical bulky boron Lewis acids (eg : trimesitylborane).

This work can be seen as stepping stones toward the synthesis of new type of catalysts. The unusual structure of the triptycene scaffold offers a wide range of functionalization pattern. It opens the possibility to tune the reactivity of 9-triptycenyloboranes by playing with various parameters such as acidity by adding electron withdrawing substituents, steric hindrance by adding bulky substituents, or chirality by adding two additional non-equivalent substituents.

For example, in addition to have a strong electron withdrawing R group, the foreseeable presence of other electron-withdrawing or bulky groups in other positions of the triptycene can lead to the obtention of strongly Lewis acidic or highly hindered boron catalyst (**Figure 20a**). Another outlook is the addition of a phosphorus atom in other positions of the triptycene (**Figure 20b**). This can lead to the synthesis of bifunctional compounds with different distances between the acidic and basic sites. Such compounds could find interesting applications as catalysts in the domain of FLP.

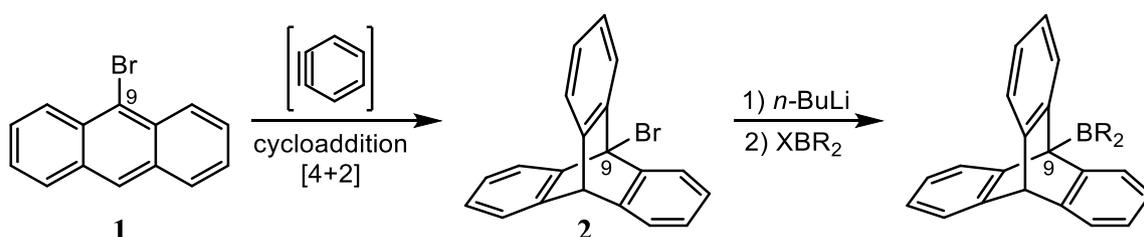


**Figure 20** – Examples of a) practicable strongly acidic or highly hindered boron catalysts and b) practicable bifunctional compounds with a boron atom in the 9-position of the triptycene.

### **3. RESULTS AND DISCUSSION**

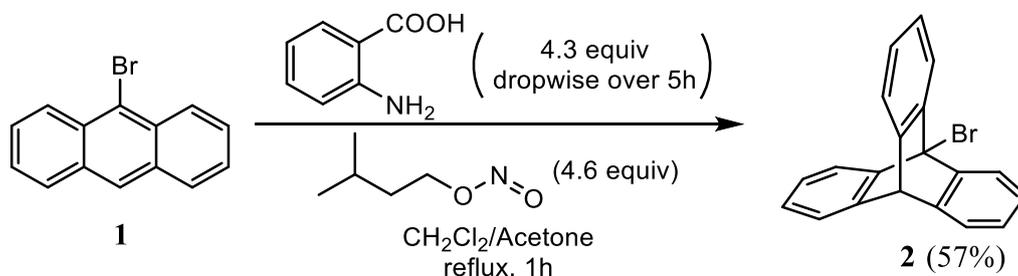
### 3.1. First pathway

The goal of our research is to use the triptycene scaffold as a very bulky substituent to synthesize completely new types of highly hindered Lewis acids. In this respect, a first synthetic pathway to reach a new family of 9-triptycenyloboronates has been developed (**Figure 21**). This involves as a first step a [4+2] cycloaddition between 9-bromoanthracene and a dienophile benzyne (generated *in-situ*). The second step consists in a Br/Li exchange on the 9-bromotriptycene precursor, followed by a borylation to obtain a triptycene substituted in the position 9 with a boron atom.



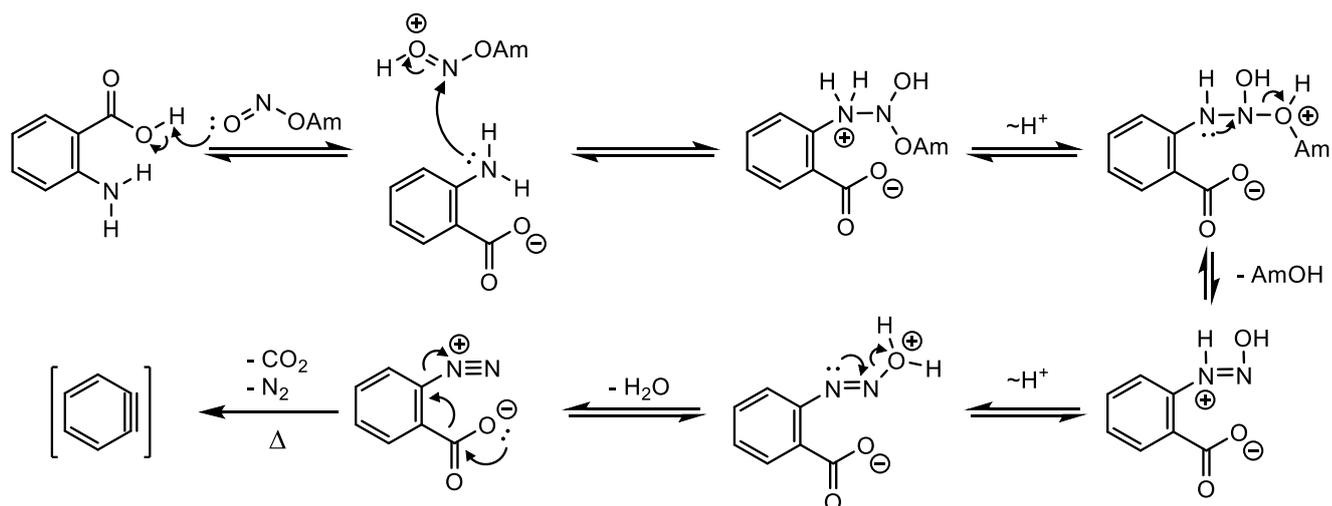
**Figure 21** – First synthetic pathway investigated for the obtention new types of highly hindered boron Lewis acids.

The first step has been set up by the optimisation of a method described in the literature<sup>[37]</sup>, affording 9-bromotriptycene in up to ten grams scale. The best condition was obtained by doing a slow benzyne generation by very slow addition of anthranilic acid in large excess on a mixture of one equiv of 9-bromoanthracene and excess isoamyl nitrite (**Figure 22**).



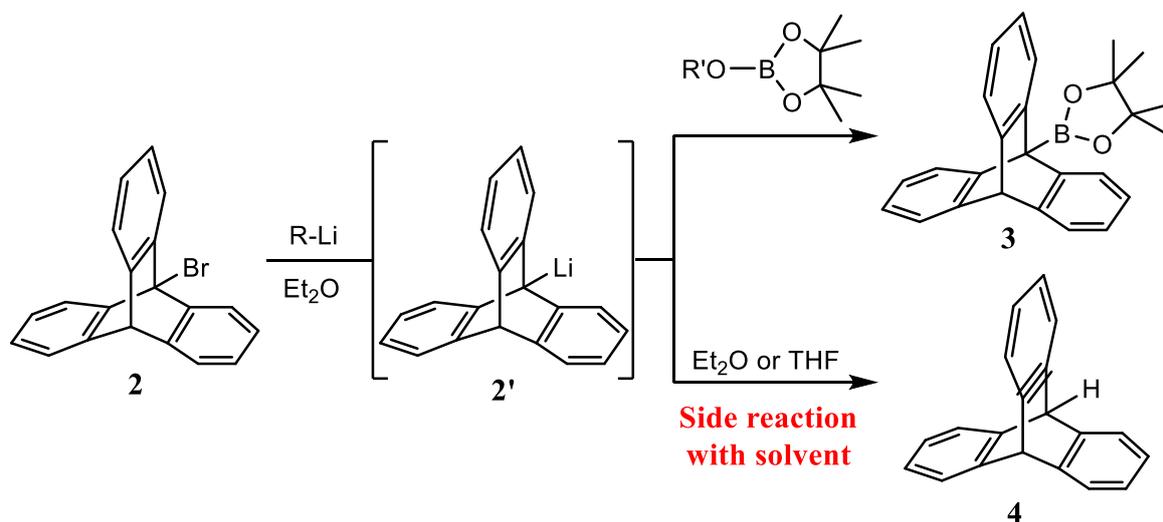
**Figure 22** – Synthesis of 2 with *in-situ* generated benzyne from anthranilic acid and isoamyl nitrite.

The moderate yield can be explained by the reactivity of the benzyne intermediate: a substantial amount is decomposing faster (by side reactions) than it reacts with 9-bromoanthracene. Therefore, using a large excess of the benzyne precursors is necessary to ensure a complete conversion of 9-bromoanthracene and performing a slow addition is needed to prevent high concentration and side reactions of benzyne. Indeed, the anthranilic acid is added on both isoamyl nitrite and 9-bromoanthracene and its reaction with this first compound generates the benzyne (**Figure 23**) which then perform the [4+2] cycloaddition on the second compound.



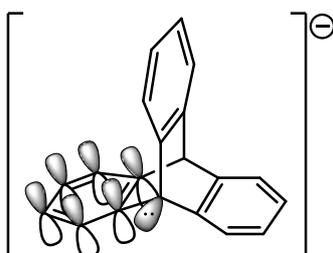
**Figure 23** – Mechanism of benzyne formation from anthranilic acid and isoamyl nitrite.

For the second step of this pathway, we first decided to use alkoxyboronic acid pinacol ester compounds as borylating reagents. Such reagents are easy to handle since they are stable liquid compounds and produce stable trivalent boron compounds thanks to the bidentate pinacol moiety. In this end, a bromine-lithium exchange on bromotriptycene **2** was performed with *n*-BuLi followed by a borylation reaction with isopropoxyboronic acid pinacol ester. The major product was triptycene **4**, indicating that triptycenylium **2'** has been generated then hydrolysed. In agreement with reported observations,<sup>[38]</sup> this is due to the very high basicity of triptycenylium which deprotonate the reaction solvent (**Figure 24**).



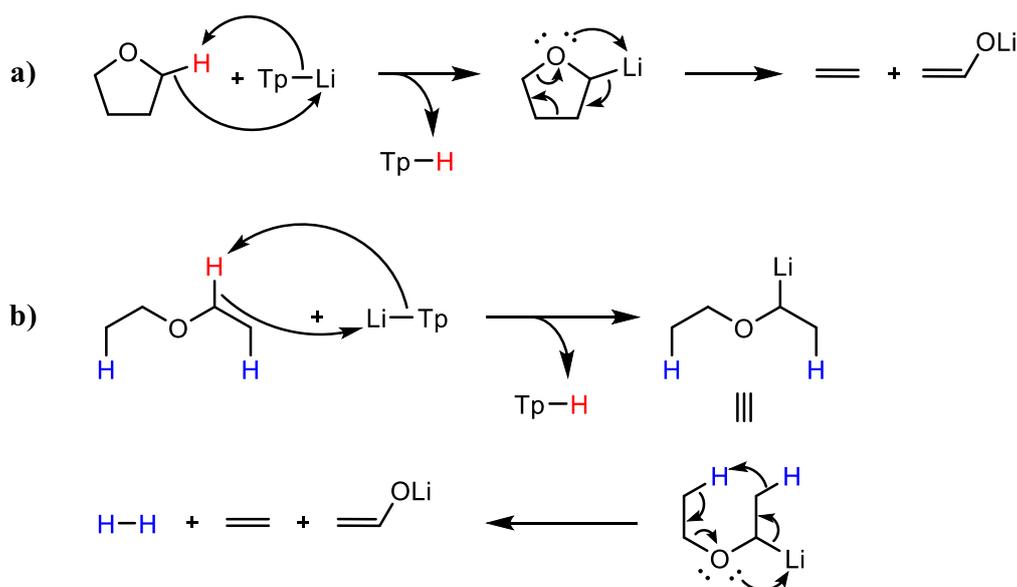
**Figure 24** – Synthesis of (9-triptycenylium)boronic acid pinacol ester **3** and formation of triptycene **4** by hydrogen abstraction from solvent.

Indeed, the basicity of triptycyl lithium **2'** results from the fact that it forms a tertiary carbanion at the bridgehead of the triptycene. The geometry of this one do not allow the stabilization of the negative charge by a delocalization on the surrounding aromatic rings. Indeed, the p-orbitals of those rings are orthogonal to the one of the lone pair of the carbanion, preventing the conjugation between them (**Figure 25**).<sup>[39]</sup>



**Figure 25** – Schematic representation of the orthogonality of the p-orbital of the aromatic rings in respect to the one of the lone pair of the carbanion.

It is therefore not surprising that the intermediate **2'** is basic enough to abstract a proton from Et<sub>2</sub>O and THF. The mechanism of both reactions is proposed below (**Figure 26**).



**Figure 26** – Proposed mechanisms for the formation of triptycene **4** by abstraction of a proton from a) THF and b) Et<sub>2</sub>O.

The lithium-bromine exchange did not proceed in unipolar tested solvents (hexane, toluene). Therefore, an optimisation of this reaction step has been carried out in order to find experimental conditions for which the triptycenylium degradation in Et<sub>2</sub>O could be limited (**Figure 24, Table 1**).

As shown in entry 1, the yield of TpBpin **3** is very low, and the major product is the decomposition product **4** showing that long lithiation time should be avoided. Thus, the temperature was allowed to increase faster (by removing the cooling bath around the Schlenk flask) to accelerate the formation of **2'**, and a slightly better yield was obtained while lithiation time has been reduced and borylation temperature has been raised to 35°C after addition (Entry 2). Entries 3 to 5 show that the lithiation step should reach room temperature after *n*-BuLi or *t*-BuLi addition, and the absence of light does not seem to be a crucial parameter (Entry 6). This excludes a radical process for the proton abstraction of **2'** from the solvent. Then the reaction using the optimised conditions (Entry 4) could afford **3** in 51% isolated yield.

*Table 1 - Conditions optimization for the formation of 9-borylated triptycene by lithiation of the 9-bromotriptycene followed by borylation.*

Entry	Lithiation conditions	Borylation conditions	Ratio TpH:TpBpin(:TpBr)	Yield of TpBpin <sup>[a]</sup>
1	<i>n</i> -BuLi (2 equiv) -94°C, 5h30	<i>i</i> -PrO-Bpin (1.5 equiv) -94°C, 10 min r.t., overnight	1.6 : 1.0	< 10 % <sup>[b]</sup>
2	<i>t</i> -BuLi (1.2 equiv) -94°C, 10 min r.t., 2h	<i>i</i> -PrO-Bpin (1.6 equiv) -94°C, 1h 35°C, overnight	0.38 : 1.0	16 %
3	<i>t</i> -BuLi (2.0 equiv) -94°C, 20 min	MeO-Bpin (1.5 equiv) -94°C, 4h r.t. overnight	2.3 : 1.0 (: 2.3)	20 % *
4	<i>t</i> -BuLi (2.0 equiv) -94°C, 1h	MeO-Bpin (1.5 equiv) -94°C, 10 min 40°C, 5h	0.30 : 1.0 (: 0.36)	61 % *
5	<i>t</i> -BuLi (1.2 equiv) -94°C, 10 min r.t., 1h	MeO-Bpin (1.5 equiv) -94°C, 10 min 40°C, 5h	0.12 : 1.0	83 %
6	<i>t</i> -BuLi (1.2 equiv) -94°C, 10 min r.t., 1h	MeO-Bpin (1.5 equiv) -94°C, 10 min 40°C, 5h	0.16 : 1.0	85 % <sup>[c]</sup>

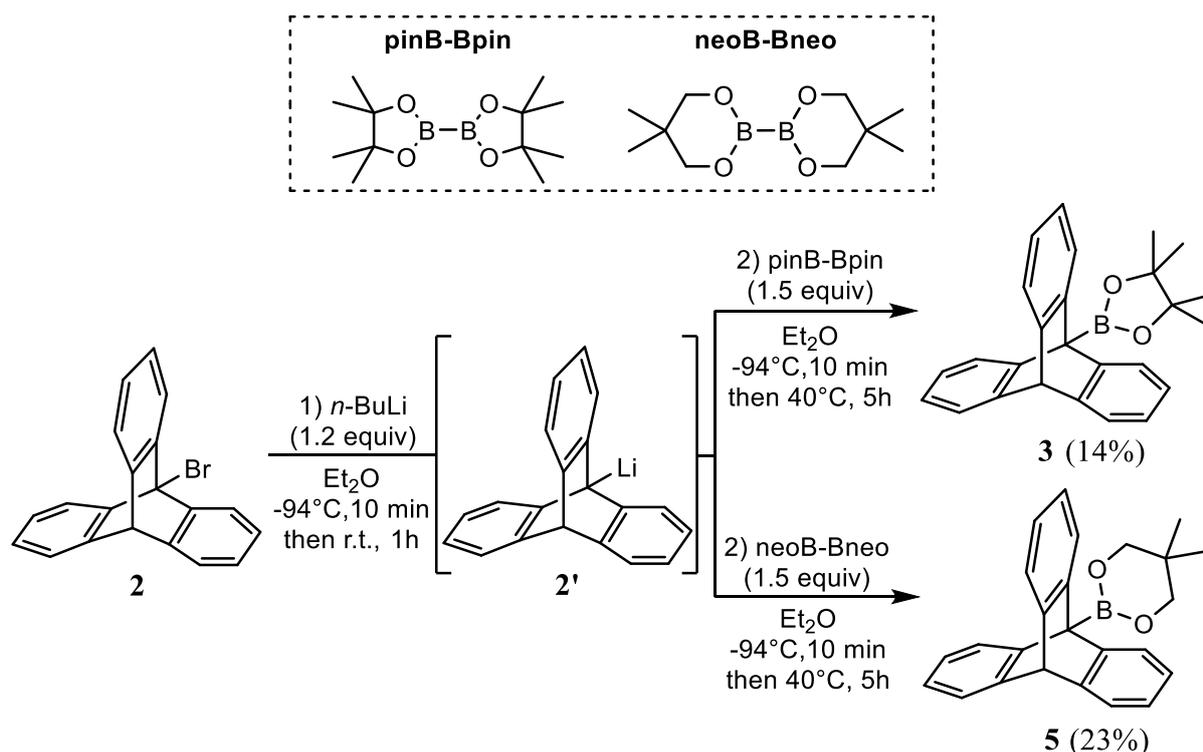
[a] Calculated from <sup>1</sup>H NMR integration.

[b] Yields decrease further in THF.

[c] Reaction performed in absence of light.

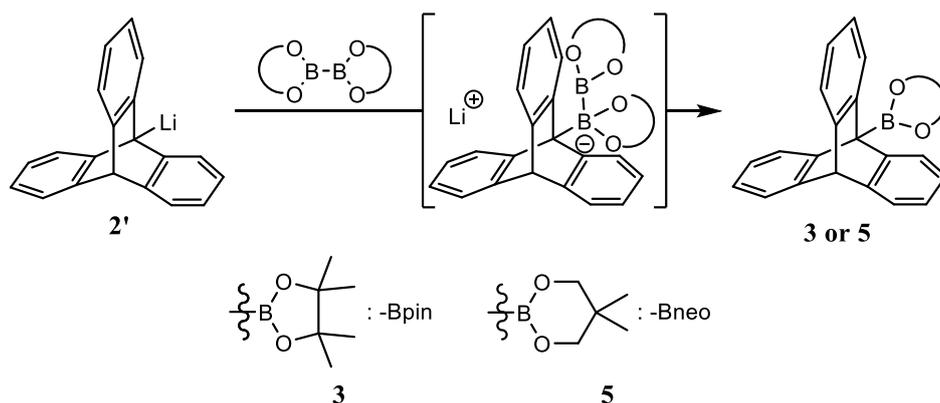
\* Recovery of 9-bromotriptycene showing that the Br/Li exchange was not completed.

In order to study the effect of the nature of the borylating agent, the borylation reaction was performed with bis(pinacolato)diboron and bis(neopentyl glycolato)diboron (**Figure 27**). Those reagents are known to be more reactive than *i*-PrOBpin or MeOBpin since the boron atom is coordinated to one less oxygen atom which provide electron back donation on boron (from their free electron pairs). The very weak boron-boron bond is also cleaved faster than the stronger boron-oxygen bond.



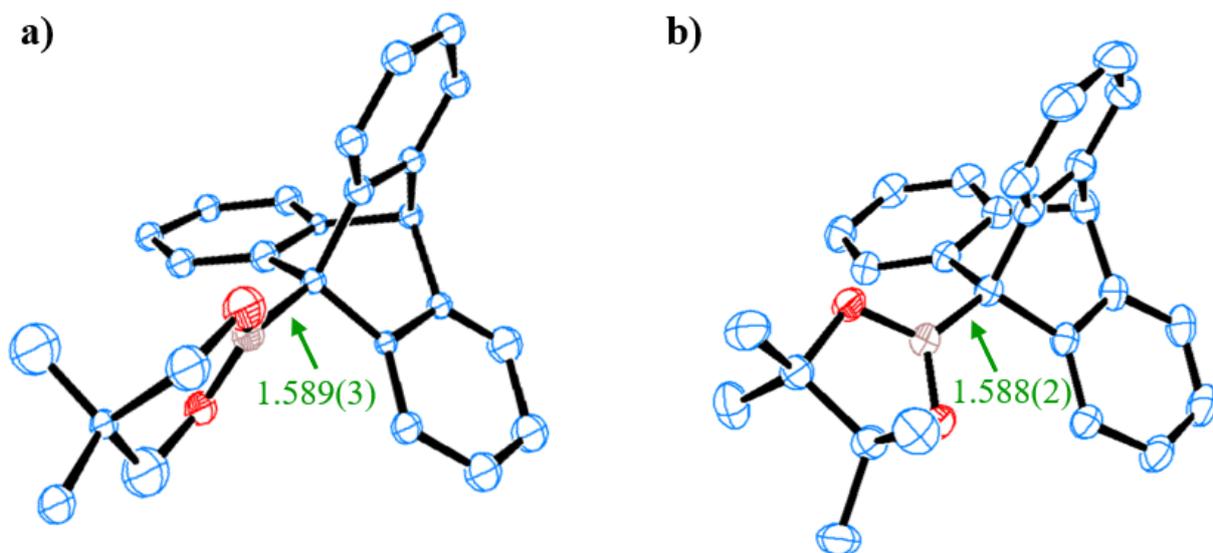
**Figure 27** – Synthesis of (9-triptycyl)boronic acid pinacol ester **4** and (9-triptycyl)boronic acid neopentyl glycol ester **5** using diboron reagents.

Low yields were obtained, thus showing that these expensive diboron reagents are not interesting, especially since half of the reagent is lost during the reaction. Steric hindrance could be responsible for such low yields (**Figure 28**). Indeed, **2'** contains a bulky triptycene scaffold and the diboron reagents have a bigger size than their alkoxy analogues RO-B(OR')<sub>2</sub>.



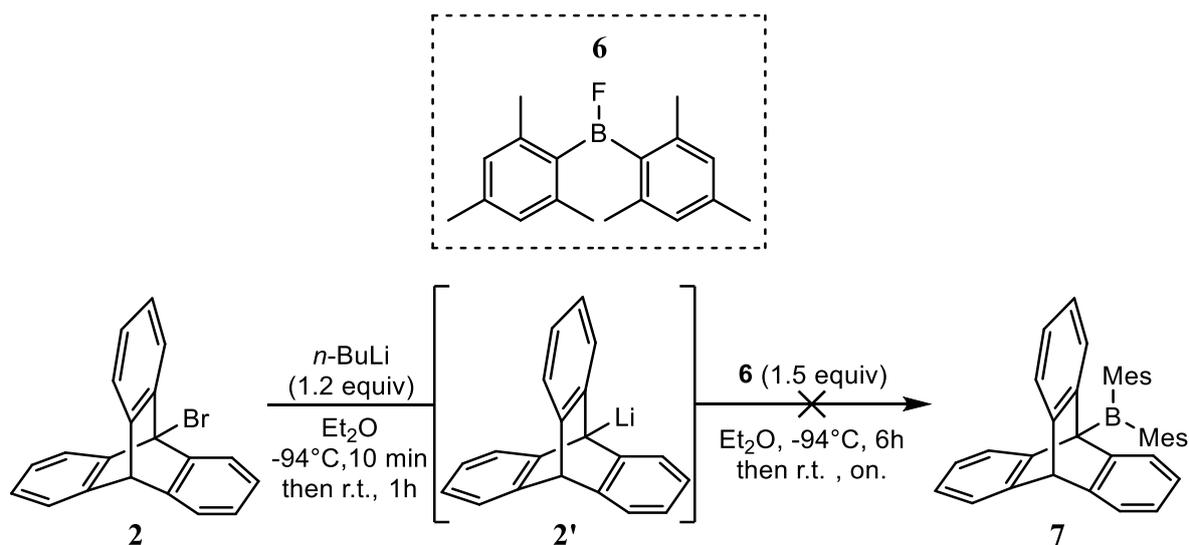
**Figure 28** – Possible steric hindrance during the synthesis of triptycenes substituted in the 9-position with a boronic acid pinacol ester moiety **3** and a boronic acid neopentyl glycol ester moiety **5**.

The X-ray structures of the products TpBneo **5** (**Figure 29a**) and TpBpin **3** (**Figure 29b**) were nevertheless determined and revealed that the C-B bond in both compounds is relatively long (1.589(3) Å for the first compound and 1.588(2) Å for the second one).



**Figure 29** – X-ray structures and C-B bond lengths in angström for the molecules of a) TpBneo and b) TpBpin.

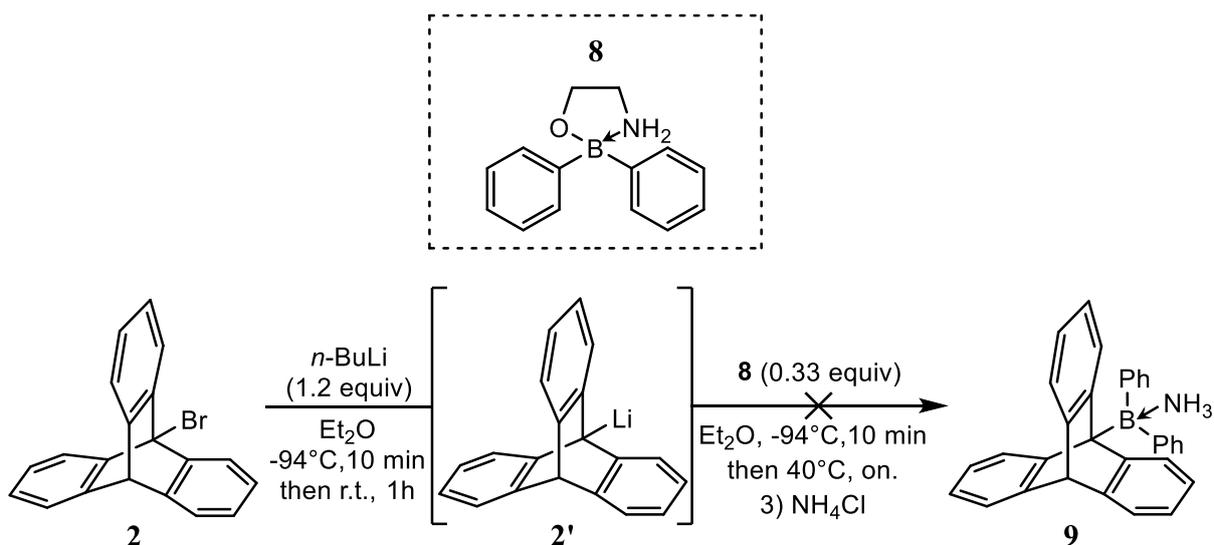
Although compound **3** and **5** are trivalent boron compounds, the presence of the two oxygens bonded to the boron atom is not a good feature to make them good Lewis acids. Indeed, as stated earlier, the oxygen atoms provide electron donation on boron from their free electron pairs. Therefore, a 9-borotriptycene with two halogen, alkyl or aryl groups on the boron atom should be stronger Lewis acids. In this aim, dimesityl boron fluoride **6** has been used as a borylating reagent (**Figure 30**). Its reaction with triptycenyllithium **2'** led to the exclusive formation of triptycene **4** via proton abstraction from Et<sub>2</sub>O.



**Figure 30** – Unsuccessful formation of compound **7** by reaction of dimesityl boron fluoride **6** with triptycyl lithium **2'**.

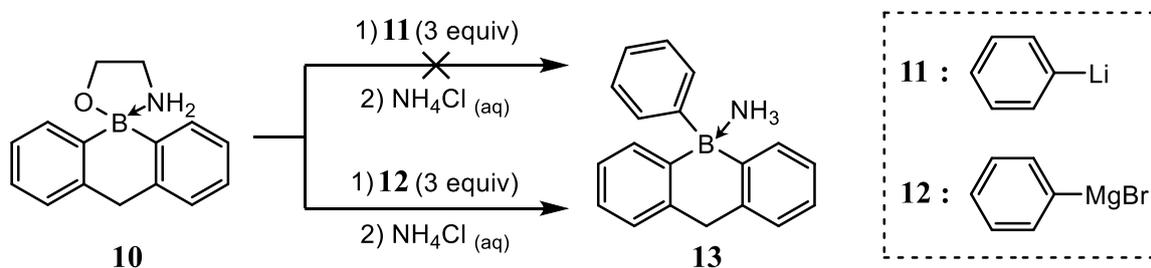
Even though dimesityl boron fluoride **6** can be used as borylation reagent for the position 1 and 2 of triptycene<sup>[34]</sup>, it seems to be too bulky to react at the bridgehead position of the triptycene scaffold. This will be further discussed (section **3.2**). In order to investigate this statement, less hindered disubstituted boron fluoride compounds could be used as borylating reagent. However, the synthesis of such compounds found in the literature were laborious or long-term ones, so that we could not obtain them.

Thus, the use of commercially available 2-aminoethyl diphenylboronate **8** as borylation reagent has been considered (**Figure 31**). On one hand, this compound contains two phenyl groups which are less hindered than the two mesityl groups present in compound **6**. On the other hand, ethanolamine bidentate ligand on the boron atom ensure the stability of the reagent. The reaction of boronate **8** with triptycyl lithium **2'** led to the exclusive formation of triptycene **4** via proton abstraction from Et<sub>2</sub>O.



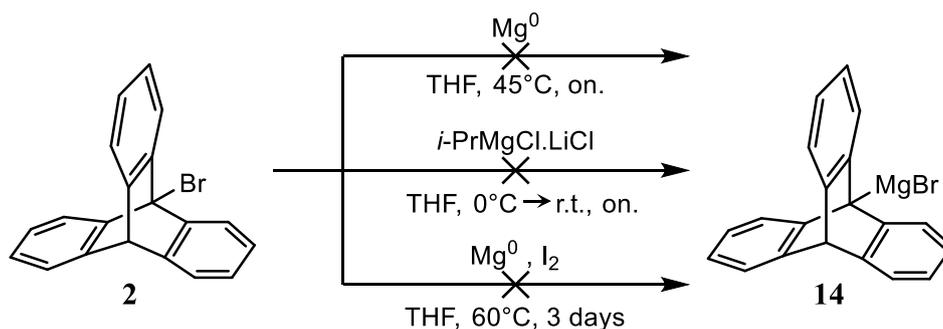
**Figure 31** - Unsuccessful formation of compound **9** by reaction of 2-aminoethyl diphenylboronate **8** with triptycyl lithium **2'**.

This last result is not surprising since there was no example in the literature of the use of **8** with a lithium compound in order to make a carbon-boron bond formation. Indeed, such reactions were only performed with organomagnesium compounds. This is in line with results obtained by Arnaud Osi for reactions of compound **10** with phenyllithium **11** and phenylmagnesium bromide **12** (**Figure 32**). The reaction led to the formation of the boronate complex **13** for three equivalents of **12** while it didn't succeed for three equivalents of **11**.



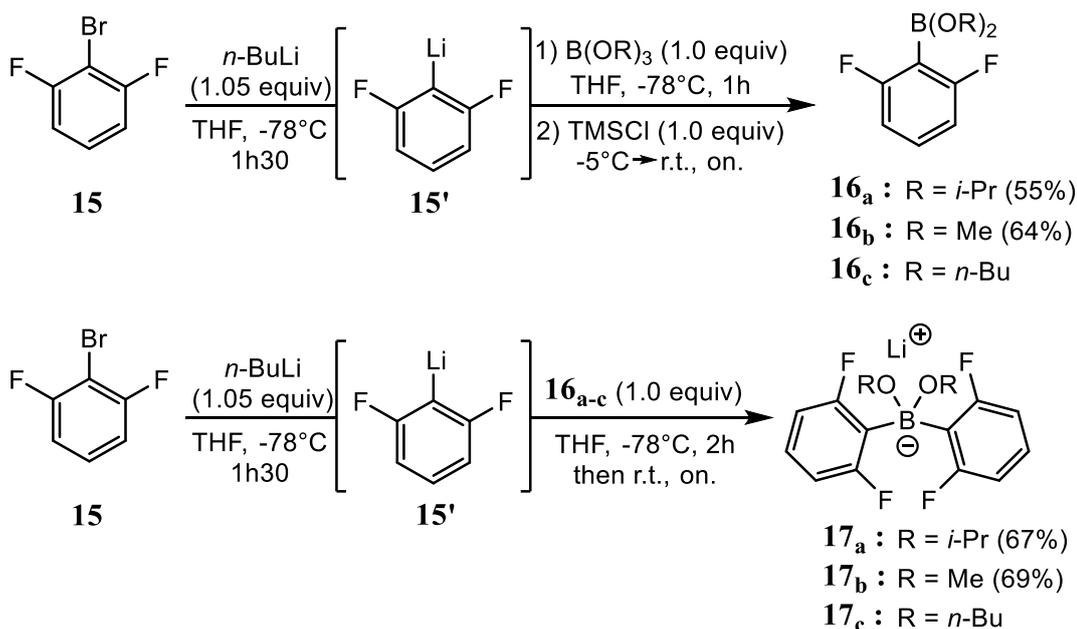
**Figure 32** – Formation of boronate complex **13** only from reaction of compound **10** with **12** and not with **11**.  
Reaction conditions : 1) THF, -94°C, 2h then r.t., overnight 2) r.t., 30min.

These results can be explained by a possible favoured boron-oxygen bond cleavage with magnesium reagents than with lithium compounds. Indeed, the complexation of the oxygen atom is stronger with magnesium than lithium.<sup>[40]</sup> Unfortunately, the formation of the organomagnesium reagent **14** from the starting 9-bromotriptycene did not proceed despite many attempts with various magnesium sources (**Figure 33**).



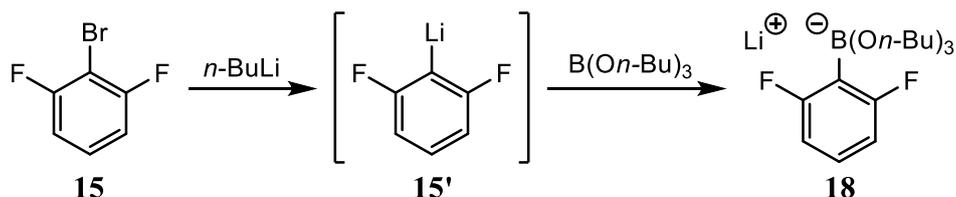
**Figure 33** – Attempts for the formation of the (9-tritriptyceny)magnesium bromide **14**.

Since the synthesis of TpBpin **3** was performed by using RO-Bpin as borylating reagents, the synthesis of RO-BAr<sub>2</sub> derivatives was considered. Reaction of such compounds with **2'** could lead to diarylated 9-borotriptycene. As mentioned earlier, the presence of fluorine atoms on the aromatic ring of arylborane derivatives increases their Lewis acidity. RO-BAr<sub>2</sub> derivatives with fluorinated aryls could be good candidates as a borylating reagent. Indeed, the boron atom is more electron deficient than in the case of RO-Bpin. Therefore, the synthesis of boronate complexes **17**<sub>a-c</sub> has been undertaken (**Figure 34**).



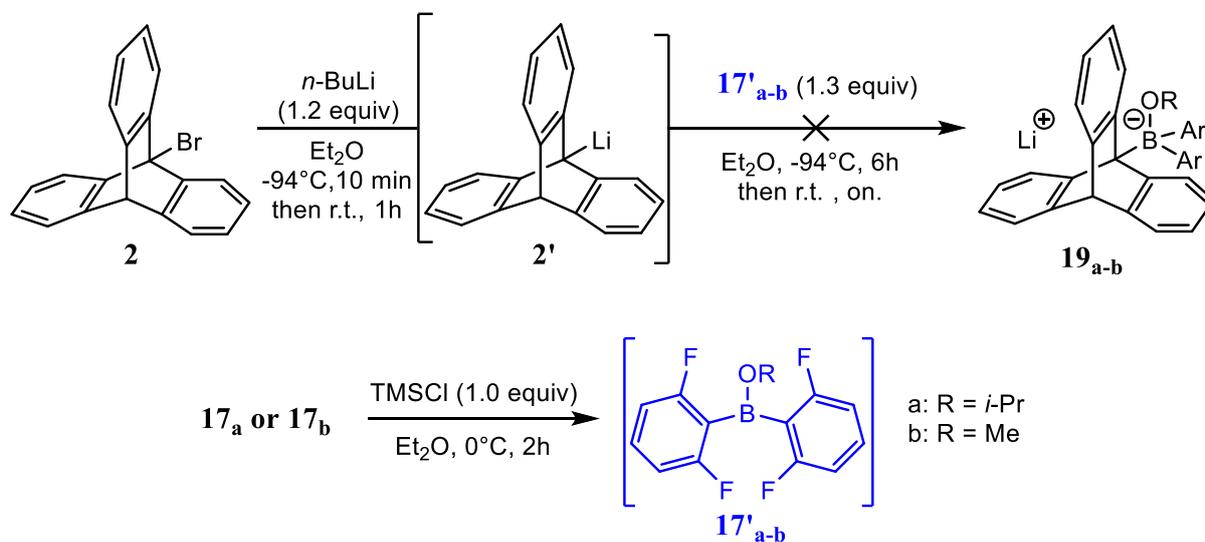
**Figure 34** – Synthesis of alkoxy diarylated boronate complexes **17**<sub>a-c</sub>.

Compounds **17<sub>a</sub>** and **17<sub>b</sub>** were isolated as boronate complexes with lithium as counter cation in order to store them as long-lived air-stable compounds. Due to the presence of unreacted tributyl borate in the crude mixture of **16<sub>c</sub>** and both compounds having a very close boiling point, a distillation did not succeed to separate them while it succeeds for the mixture of **16<sub>a</sub>** and **16<sub>b</sub>** with their trialkyl borate analogues. Since compound **16<sub>c</sub>** could not be isolated as a pure product, a side reaction during the synthesis of **17<sub>c</sub>** was observed to produce the side product **18** (*Figure 35*).



*Figure 35* – Formation of **18** by a side reaction of **15'** with tributyl borate during the synthesis of **17<sub>c</sub>**.

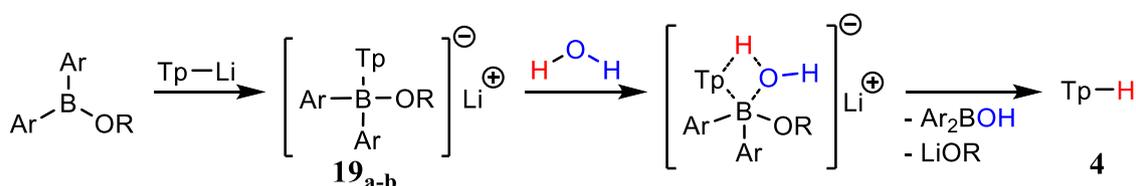
Compound **17<sub>c</sub>** and the side product **18** could neither be separated. Therefore, the reactions of **2'** with **17<sub>a</sub>** and **17<sub>b</sub>** after treating them with trimethylsilyl chloride were undertaken (*Figure 36*).



*Figure 36* – Unsuccessful formation of compounds **19<sub>a-b</sub>** using **17'<sub>a</sub>** or **17'<sub>b</sub>** on triptycyl lithium **2'**.

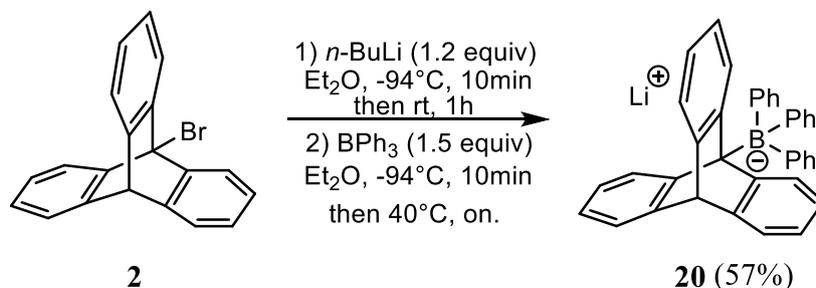
After evaporation of the solvents, products **19<sub>a-b</sub>** were not formed and triptycene **4** was recovered as a product of the side reaction of **2'** with  $\text{Et}_2\text{O}$ . This indicates that the reaction of **17'<sub>a</sub>** or **17'<sub>b</sub>** with **2'** does not occur or is very slow compared to the hydrogen abstraction of **2'** with the solvent. The favourable electrophilic character of the borylating reagent is perhaps countered by the steric hindrance of the two arylated groups, apparently higher than the pinacol

moiety. The steric hindrance can also be induced by the presence of the fluorine atoms in *ortho* position. While in *ortho* position, the fluorine electron density will be located near the boron atom and can prevent the attack of a nucleophile that will not be able to get close enough to the reactive centre of the electrophile. In order to check this assumption, the synthesis of alkoxy fluorodiarylated boron derivatives with no substituents in *ortho* position of the aryl groups should be undertaken. In this way, the reaction of **2'** with less sterically hindered borylating reagents than the **17'** derivatives could be investigated, for example with the fluorine atoms in *para* position. Another explanation than steric hindrance can be considered according to reported observations for compounds of a similar nature.<sup>[41]</sup> Compounds **19<sub>a-b</sub>** could have been formed and then hydrolysed during the mixture treatment either by the water present in the solvents or in the air. Such process could also lead to the formation of triptycene **4** (**Figure 37**).



**Figure 37** – Possible side reaction of products **19<sub>a-b</sub>** with water to form triptycene **4** as a side product.

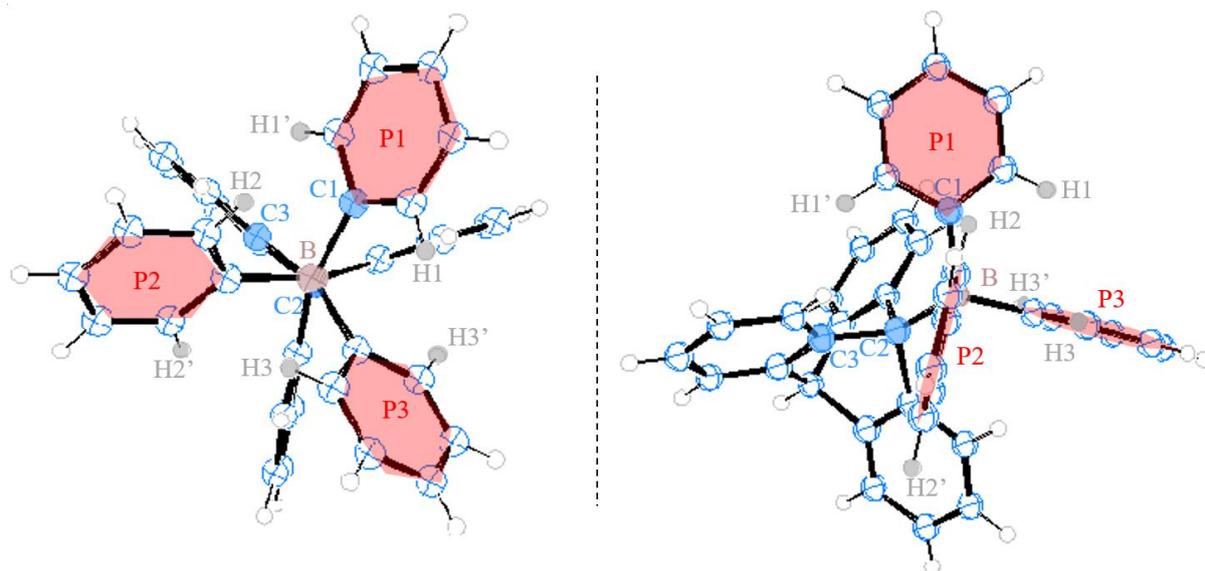
These results are puzzling since the addition of triphenylborane on triptycenylium was reported by Wittig<sup>[35]</sup> and was reproduced by us to obtain **20** in 57% yield (**Figure 38**).



**Figure 38** – Synthesis of lithium (9-triptycenylium)triphenylborate **20**.

A X-ray diffraction structure of the tetravalent boron anion present in **20** has been published<sup>[42]</sup> with ammonium as a counter cation and is presented with two different sides of view (**Figure 39**). The planes (P1, P2 and P3) of the phenyl rings connected to the boron atom do not intersect along the C<sub>2</sub>-B bond axis as it is the case for the ones of the aromatic rings of the triptycene scaffold. Such a feature allows to reduce a steric repulsion between H1, H2 and H3 which would have pointed toward each other if P1, P2 and P3 intersected along the considered axis. As a consequence of this feature, the phenyl groups on the boron atom are staggered with respect to the aromatic rings of the triptycene scaffold with a C<sub>1</sub>-B-C<sub>2</sub>-C<sub>3</sub> dihedral angle of -78.3°. Such an angle allows to reduce the steric effect between hydrogen atoms H1', H2', H3' and the aromatic rings of the triptycene scaffold. The structure of the triphenylborane allows to avoid the steric hinderance that could occur during the reaction of the triptycenylium lithium **2'** and the borylating agent. This points out the fact that the structure of the latter is an important factor toward the obtention of 9-borylated triptycene derivatives from triptycenylium lithium **2'**.

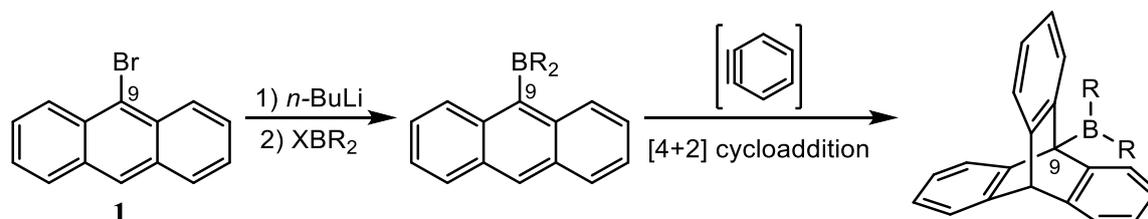
In order to investigate the influence of the presence of fluorine atoms on the borylating agent, the use of tris(pentafluorophenyl)borane should be carried out.



**Figure 39** - Two different sides of view of the X-ray diffraction structure of the tetravalent boron anion present in **20**.

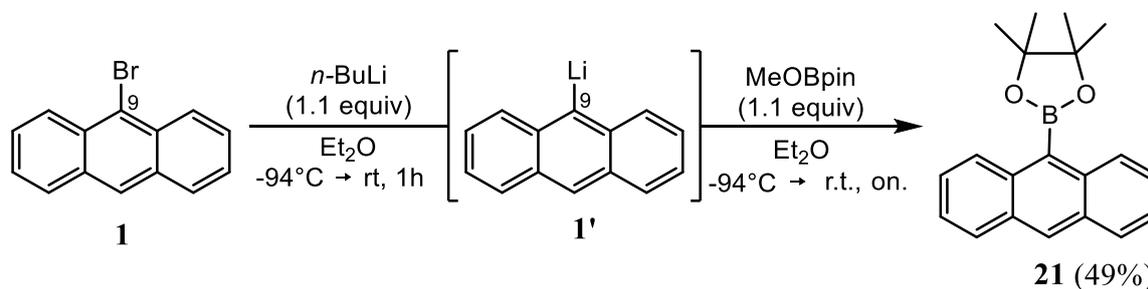
### 3.2. Second pathway

The second synthetic approach (**Figure 40**) involves as a first step the Br/Li exchange on bromoanthracene **1** followed by borylation to afford a 9-boron substituted anthracene. The second step is the [4+2] cycloaddition on this resulting 9-boroanthracene with a dienophile benzyne (generated *in situ* from anthranilic acid and isoamyl nitrite).



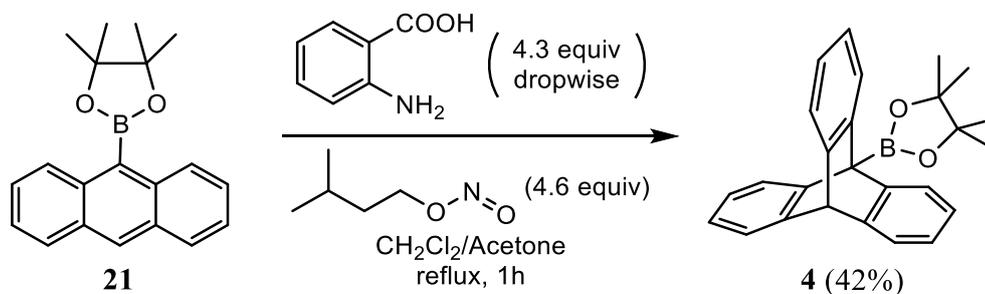
**Figure 40** – Second synthetic pathway investigated for the obtention of new types of highly hindered boron Lewis acids.

This pathway goes through a Br/Li exchange on **1** leading to the formation of 9-anthracenyl lithium **1'** in the first step. The latter is not basic enough to deprotonate Et<sub>2</sub>O. In this way, the formation of a considerable amount of side product is expected to be avoided. The Br/Li exchange on **1** followed by borylation reaction with MeOBpin produced **21** in 49% isolated yield (**Figure 41**).



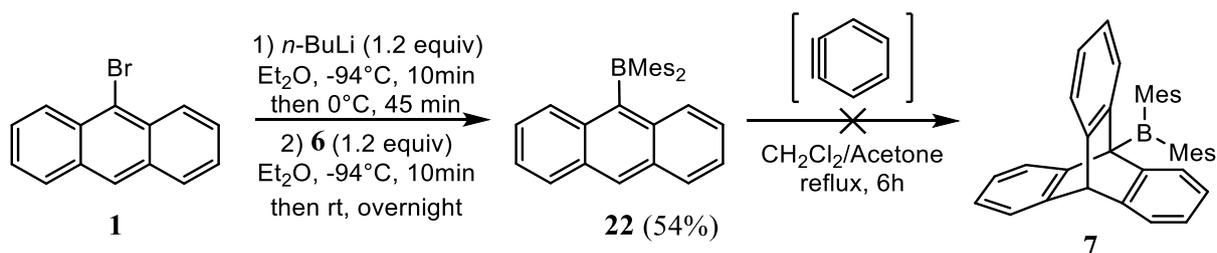
**Figure 41** – Synthesis of (9-anthracenyl)boronic acid pinacol ester **21**.

Then a [4+2] cycloaddition was performed on **21** with a dienophile benzyne (generated *in situ* from anthranilic acid and isoamyl nitrite) to obtain **4** in a 42% yield (**Figure 42**).



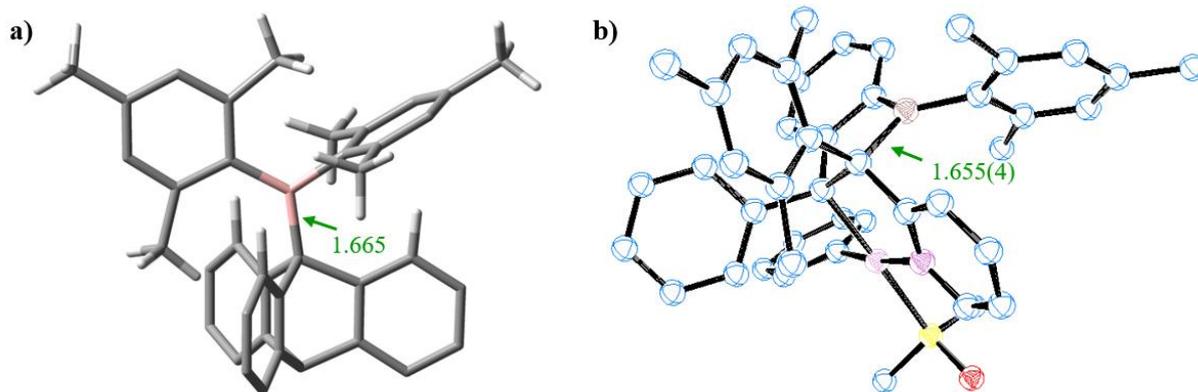
**Figure 42** – Synthesis of (9-triptyceny)boronic acid pinacol ester **4**.

Cycloaddition with very reactive benzyne intermediate can be effective toward reactions involving steric effect issues such as with *t*-Bu substituted anthracene<sup>[43]</sup>. The synthesis of **7** has been investigated by doing a [4+2] cycloaddition on **22**, obtained in 54% yield from **1** by Br/Li exchange and borylation reaction using dimesityl boron fluoride **6** (**Figure 43**). <sup>1</sup>H NMR analysis of the crude reaction mixture revealed that the [4+2] cycloaddition could not afford **7**. The products of the reaction were aromatic compounds, obviously derived from benzyne side reactions, and the anthracene **22** could be detected in large amount indicating that this compound may be inert to the [4+2] cycloaddition under mild conditions.



**Figure 43** – Synthesis of (9-anthracenyl)dimesitylborane **22** and [4+2] cycloaddition attempt to afford **7**.

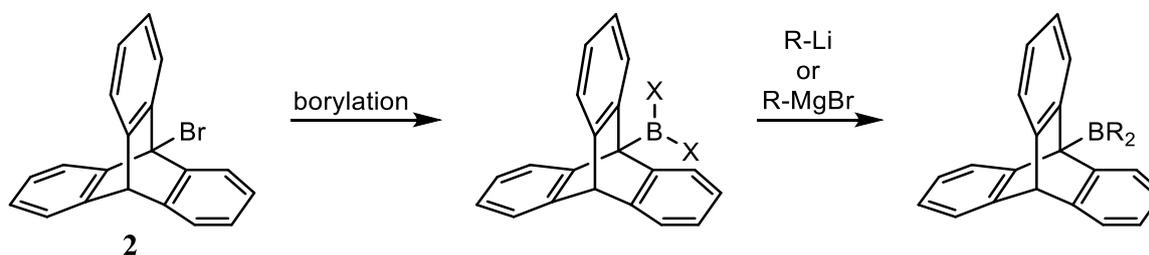
The formation of **7** may be possible with harder conditions, for example by increasing the temperature. However, results from structural calculations suggest that the reaction may not be possible due to steric hindrance: the theoretical structure obtained for compound **7** from geometry optimisation show a 1.665 Å bond distance between the boron atom and the bridgehead carbon of the triptycene (**Figure 44a**). This can explain why the formation of **7** did not proceed since such a long distance is very unusual for similar compounds. Indeed, 1.655(4) Å is the distance of the longest B-C(sp<sup>3</sup>) bond found in the Cambridge Crystallographic Data Center for a trivalent boron compound in which there is one B-C(sp<sup>3</sup>) and two B-C(sp<sup>2</sup>) bonds (**Figure 44b**). Most of the other longest distances for a B-C(sp<sup>3</sup>) for such compounds were smaller than 1.600 Å.



**Figure 44** – Structures and B-C( $sp^3$ ) bond lengths in angström of a) (9-triptycenyldimesitylborane) obtained from theoretical geometry optimisation and b) of the trivalent boron compound containing the longest B-C( $sp^3$ ) bond obtained from crystallographic data.

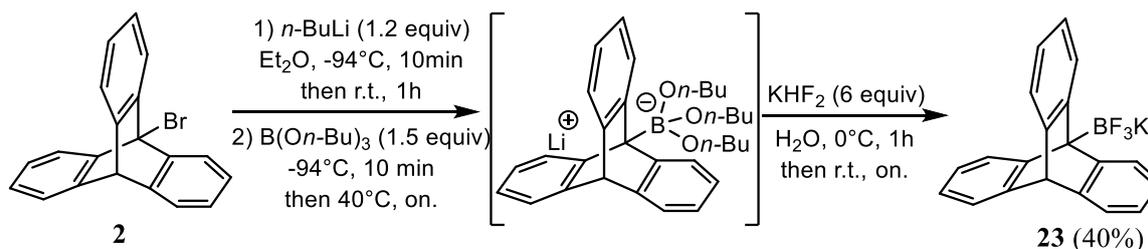
### 3.3. Synthesis via stable 9-boron triptycene intermediates

This alternative route involves, as a first step, the use of a highly reactive boron agent on triptycenylium **2'** in order to limit the formation of side product triptycene **4** and to obtain a 9-boron triptycene with boron ligands which can be substituted by a nucleophile, as a second step (**Figure 45**).



**Figure 45** – Third synthetic pathway investigated for the obtention of new types of highly hindered boron Lewis acids.

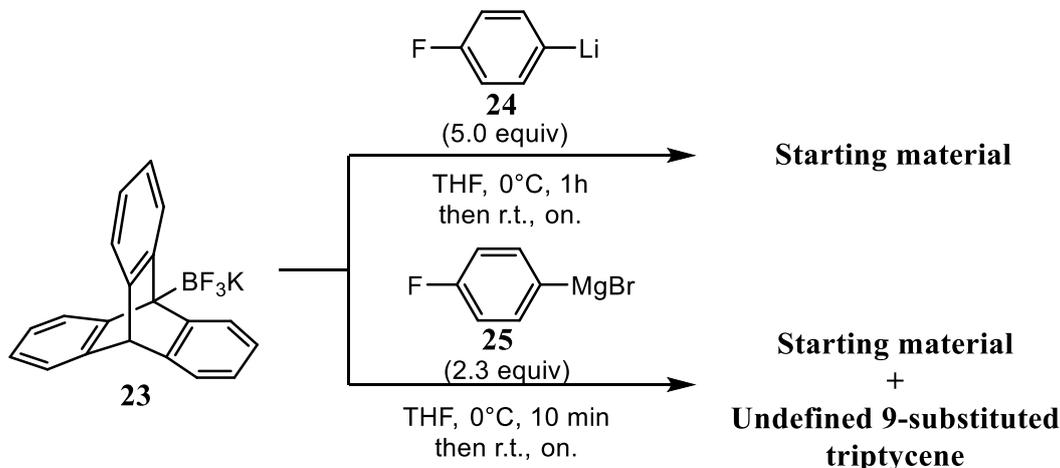
Organotrifluoroborate salts are air stable compounds reactive toward nucleophiles and they can be obtained by a one-step procedure using trialkylborate as borylating agent. They appear to be good candidates as intermediates for the foregoing suggested strategy. Therefore, the synthesis of potassium (9-triptycenylium)trifluoroborate from 9-bromotriptycene was undertaken to afford **23** in 40% yield (**Figure 46**).



**Figure 46** – Synthesis of potassium (9-triptyceny)trifluoroborate **23**.

Trifluoroborate **23** can therefore be used as a reactant in order to obtain arylated boron triptycene. In this respect, its reaction with aryllithium compound and arylated organomagnesium compounds was investigated.

When the reaction with parafluorophenyllithium **24** (5 equiv) was carried overnight at room temperature, only the starting material was recovered. With the use of organomagnesium reagent **25** (2.3 equiv), NMR analysis of the crude reaction revealed that, in addition to the starting material, another 9-substituted triptycene species, characterized by a typical signal pattern, was observed (**Figure 47**). Thus, organomagnesium reagents seems to be more reactive toward **23** and future synthetic efforts should be devoted to this method.



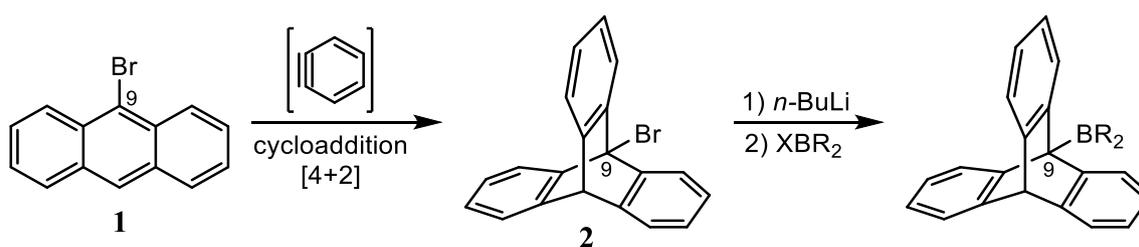
**Figure 47** – Reaction of **23** overnight at room temperature with a) 5 equivalents of aryllithium **24** and b) 2.3 equivalent of organomagnesium reagent **25**.

## **4. CONCLUSION AND PERSPECTIVES**

## 4.1. Conclusion

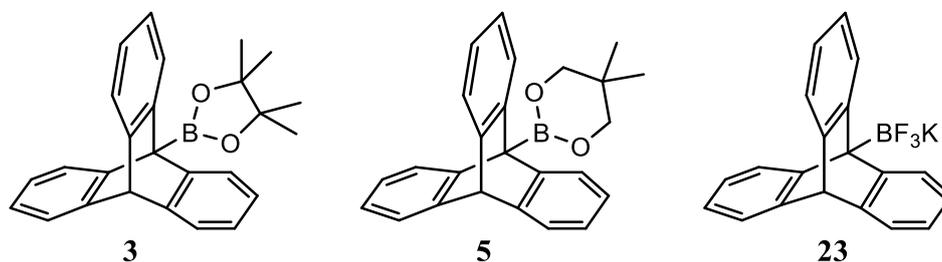
Boron Lewis acids are widely used as activators and catalysts in organic chemistry. The design and development of new types of sterically hindered boron Lewis acids are highly awaited for opening new synthetic possibilities in emerging areas of catalysis (eg: FLP chemistry) and materials science (eg: anion detectors). Therefore, the insertion of a boron substituent on the position 9 of the triptycene has been studied in this master work in order to obtain a bulky trivalent boron Lewis acid. The triptycene framework has been chosen for its interesting properties. Indeed this scaffold has a rigid and bulky structure. What's more, it shows a lot of functionalizable positions which can be interesting for the investigation of further outlook.

The first method which was developed consisted in a lithiation/borylation of 9-bromotriptycene obtained from a [4+2] cycloaddition between 9-bromoanthracene and a dienophile benzyne (**Figure 48**).



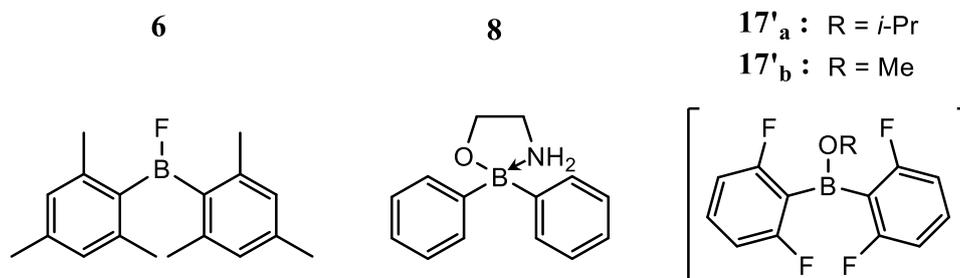
**Figure 48** – First synthetic pathway investigated.

We were able to find optimal Br/Li exchange conditions to minimize the reaction of the triptycenylium intermediate with the ethereal solvent. Three new triptycenylium boron derivatives were obtained (**Figure 49**).



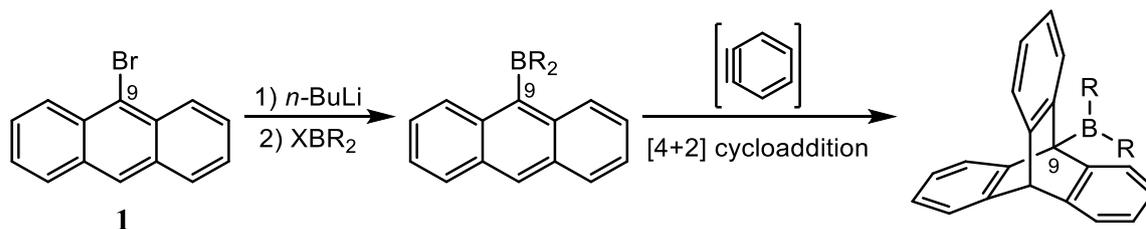
**Figure 49** – New 9-triptycenylium boron derivatives obtained thanks to the first pathway.

Though they are not good Lewis acids, they constitute important substrate for reaching stronger boron Lewis acids derived from triptycene. This seems to remain the best chance to succeed to synthesize very hindered Lewis acids since the use of arylated boron electrophiles such as dimesityl boron fluoride **6**, 2-aminoethyl diphenylboronate **8** and alkoxy di-ortho-fluorodiarylated boron compounds **17'**<sub>a-b</sub> (**Figure 50**) showed unsuccessful results.



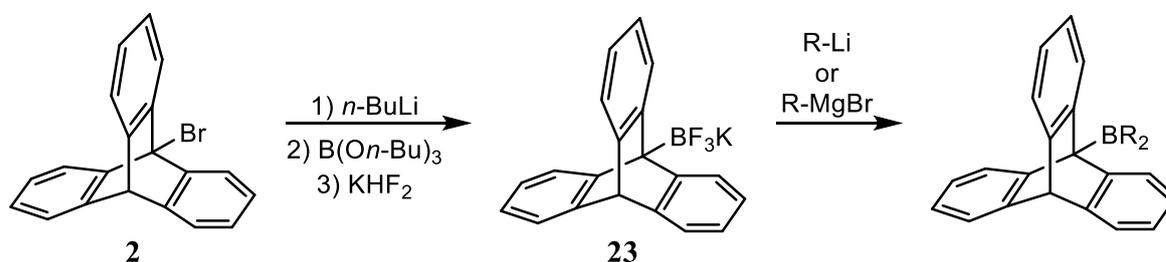
**Figure 50** – Borylating agents that did not react with triptycenylium **2'**.

The second method which was developed is based on a key [4+2] cycloaddition step between a borylated anthracene and a dienophile benzyne (**Figure 51**). Though the reaction on Anth-Bpin **21** gave good results, the Anth-BMe<sub>2</sub> **22** was unreactive.



**Figure 51** – Second synthetic pathway investigated.

The third method attempted was the use of trifluoroborate salt **23** as starting material for a substitution on the boron atom with strong organometallic reagents (**Figure 52**).

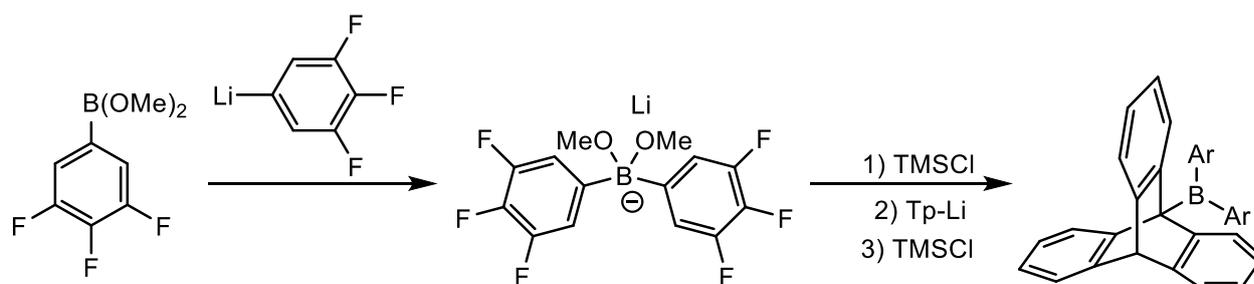


**Figure 52** – Third synthetic pathway investigated.

The current reactions did not afford results allowing genuine conclusions. More investigations on this strategy must be carried out.

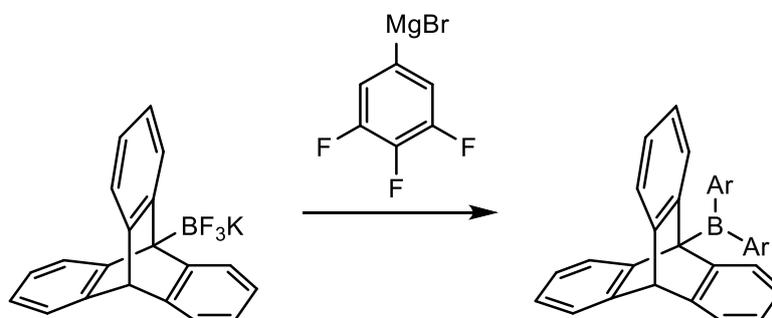
## 4.2. Perspectives

Several advanced intermediates toward the synthesis of a completely new type of hindered Lewis acid of a  $\text{TpBAr}_2$  structure have been obtained. We can hypothesize that the use of poly-fluorinated alkoxy boron derivatives with no substituents in *ortho* position of the aryl groups can provide 9-tryptycenyl diarylated boron compounds (**Figure 53**).



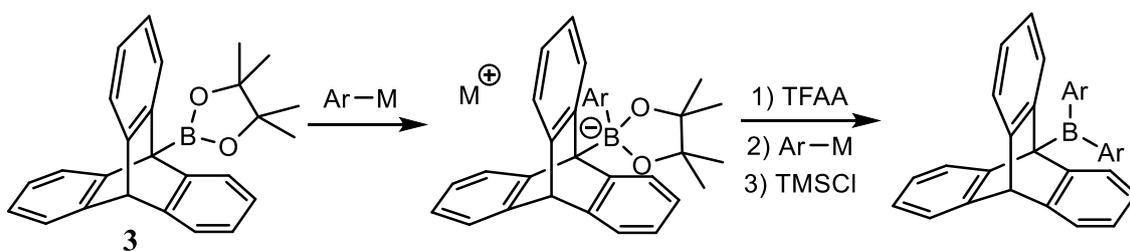
**Figure 53** – Strategy considered for the obtention of diarylated 9-borotryptycene.

The second strategy that is worth of investigation is the reaction of organomagnesium reagent with trifluoroborate salt **23** in order to find optimized conditions for total conversion of the starting product and direct obtention of trivalent boron compounds (**Figure 54**). For example, high temperature and longer reaction time can be tested.



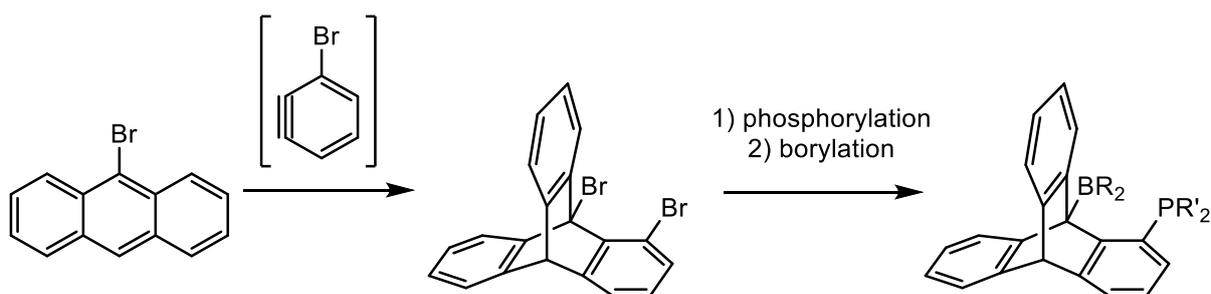
**Figure 54** - Strategy considered for the obtention of diarylated 9-borotryptycene.

We can also consider the reaction of an arylated organometallic compound with  $\text{TpBpin}$  **3** as starting material in order to make a mono addition of this last. The resulting boronate complex can be opened with an electrophile such as trifluoroacetic anhydride before the addition of another arylated organometallic compound (**Figure 55**).



**Figure 55** - Strategy considered for the obtention of diarylated 9-borotriptycene.

The second outlook of this master work can be the synthesis of bifunctional catalysts. Indeed, triptycenes with phosphino group on the aromatic rings have already been reported.<sup>[33]</sup> Our results may be applied to the lithiation/borylation of phosphino substituted triptycene for the insertion of a boron substituent at the bridgehead position. The starting triptycene derivative could be obtained by performing a [4+2] cycloaddition reaction with 3-bromobenzene on 9-bromoanthracene followed by phosphorylation. Then, a borylation could lead to the final bifunctional compound (**Figure 56**).



**Figure 56** – Synthetic pathway affording phosphino triptycene with bromine atom in the position 9 of the triptycene.

## **5. EXPERIMENTAL SECTION**

## 5.1. General methods

All reactions were carried under argon atmosphere and flasks were dried under vacuum with a heating gun using usual Schlenk techniques.

All solvents were dried with a solvent purification system. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, Carbosynth, FluoroChem and TCI and used without further purification.

Single-crystal diffraction of molecules **3** and **5** were collected on an Oxford Diffraction Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by SHELXT and then refined by full-matrix least-squares refinement of  $|F|$  using SHELXL-2016. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located from a difference Fourier map. Hydrogen atoms not involved in hydrogen bonding were refined in the riding mode with isotropic temperature factors fixed at 1.2U of the parent atoms (1.5U for methyl group). Coordinates of the hydrogen atoms implicated in hydrogen bonds were refined.

All the NMR samples were prepared in a standard 5 mm borosilicate tube at room temperature (between 18 and 22 °C) by diluting the sample in deuterated solvents. Spectra were resolved with MestReNova program. The coupling constants ( $J$ ) are given in Hertz (Hz). The chemical shifts of signals featuring defined multiplicity were determined by the arithmetic mean of the signal lines. Therefore, the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet and their combinations.

### 5.1.1. $^1\text{H}$ NMR

Spectra were recorded on a JEOL JNM EX-400 at 400 MHz. Chemical shifts ( $\delta$ ) are given in ppm referring to the partially deuterated nuclei of the used solvents (7.26 for chloroform- $d$ , 2.50 for DMSO- $d_6$  and 1.94 for acetonitrile- $d_3$ ).

### 5.1.2. $^{13}\text{C}$ NMR

Spectra were recorded on a JEOL JNM EX-400 at 100 MHz. Chemical shifts ( $\delta$ ) are given in ppm referring to the partially deuterated nuclei of the solvent used (77.16 for chloroform- $d$  and 39.52 for DMSO- $d_6$ ). All spectra are decoupled from hydrogen.

### **5.1.3. <sup>11</sup>B NMR**

Spectra were recorded on a JEOL JNM EX-400 at 160 MHz. Chemical shifts ( $\delta$ ) are given in ppm and are uncorrected.

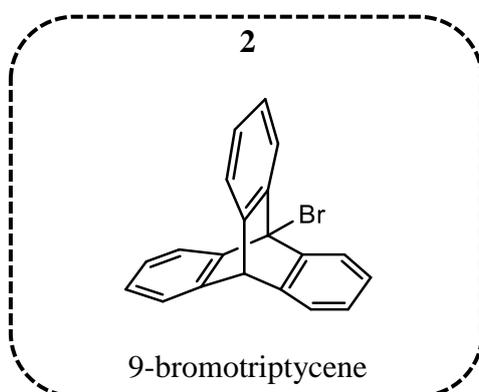
### **5.1.4. <sup>19</sup>F NMR**

Spectra were either recorded on a JEOL JNM EX-400 at 377 MHz. Chemical shifts ( $\delta$ ) are given in ppm and are uncorrected. All spectra are decoupled from hydrogen.

### **5.1.5. Flash chromatography**

Flash chromatographies were performed on silica gel using Davisil® (particle size 40-63  $\mu\text{m}$ , 60 A) in usual conditions ( $\pm 30$  g of silica/alumina for 1 g of crude). Solvents were at least of technical grade. The indicated mixture ratios are given as volumic percentages.

## 5.2. Synthetic procedures and characterizations



**Chemical formula :** C<sub>20</sub>H<sub>13</sub>Br

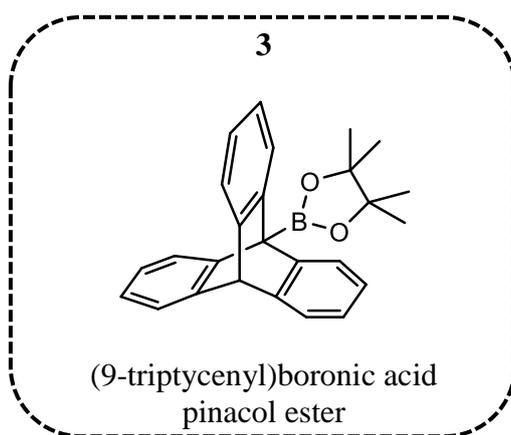
**Molecular weight :** 333.23 g.mol<sup>-1</sup>

Prepared according to a modified literature procedure.<sup>(1)</sup> In a 500 mL three necked flask equipped with a reflux condenser and a dropping funnel was added 9-bromoanthracene (5.01 g, 19.5 mmol, 1.0 eq) as well as isoamyl nitrite (12.0 mL, 90 mmol, 4.6 eq) in CH<sub>2</sub>Cl<sub>2</sub> (75 mL). In the dropping funnel was added anthranilic acid (11.5 g, 83.9 mmol, 4.3 eq) dissolved in acetone (100 mL). The flask is warmed to 60°C and the dropping funnel contents were added dropwise under stirring during a period of 5h. The reaction mixture is then stirred for an additional hour at 60°C. The solvents were removed under reduced pressure to give a black oily residue. Impurities are dissolved in MeOH (50 mL) and a filtration followed by washing with MeOH (3x15 mL) afforded the pure product as a yellow powder (3.68 g, 57%). <sup>1</sup>H NMR data were in agreement with the literature.

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 7.83-7.81 (m, 3H), 7.41-7.40 (m, 3H), 7.09-7.07 (m, 6H), 5.46 (s, 1H).

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 144.4, 143.7, 126.4, 125.48, 123.91, 123.12, 71.5, 53.7 .

<sup>(1)</sup> Y. Kawada & H. Iwamura, *J. Am. Chem. Soc.* **1983**, 105, 1449-1459



**Chemical formula :** C<sub>26</sub>H<sub>25</sub>BO<sub>2</sub>

**Molecular weight :** 380.29 g.mol<sup>-1</sup>

In a 50 mL Schlenk flask was added 9-bromotriptycene (200 mg, 0.602 mmol, 1.0 eq) in suspension in dry Et<sub>2</sub>O (15 mL). The flask is cooled to -94°C thanks to an acetone/N<sub>2(l)</sub> bath and *n*-butyllithium (0.30 mL, 2.5 M in hexanes, 0.75 mmol, 1.2 eq) was added dropwise under vigorous stirring. 10 min after the addition, the bath is removed to allow the reaction to warm up at r.t. and the reaction is stirred for an additional hour. The reaction mixture is then cooled again to -94°C and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.15 mL, 0.89 mmol, 1.5 eq) is added. 10 min after addition, the bath is removed and the flask is equipped with a reflux condenser and the mixture is warmed to 40°C and stirred for 5h. The reaction is quenched with water (10 mL). The combined organic layers are extracted with EtOAc (3x10 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product is purified by flash chromatography using cyclohexane/EtOAc (90:10) as an eluant affording the pure product as a slightly brown powder (118 mg, 51%). Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of **3** in EtOAc.

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 7.82-7.79 (m, 3H), 7.38-7.35 (m, 3H), 6.99-6.97 (m, 6H), 5.35 (s, 1H), 1.63 (s, 12H).

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 147.0, 146.61, 146.60, 134.3, 127.4, 123.6, 84.5, 55.1, 25.8 .

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 33.4 (br).

## X-ray structure of compound 3

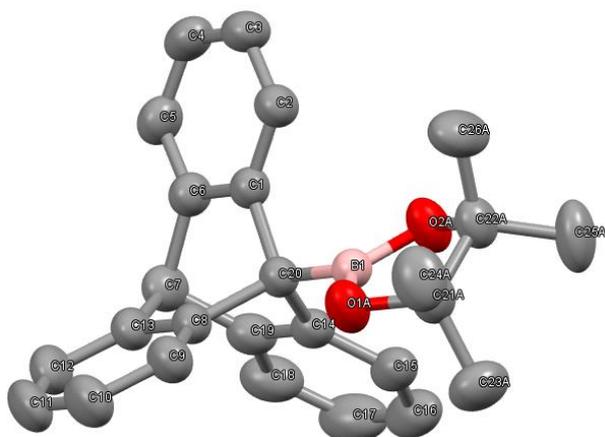


Figure 57 – X-ray structure of compound 3.

**Crystal system** : Orthorhombic

**Space group** : P b c a

**a** : 16.5002(3)      **b** : 12.02774(17)      **c** : 21.0103(3)

**$\alpha$**  : 90°       **$\beta$**  : 90°       **$\gamma$**  : 90°

**V** : 4169.71 Å<sup>3</sup>

**Z** : 8

**R-Factor** : 4.18 %

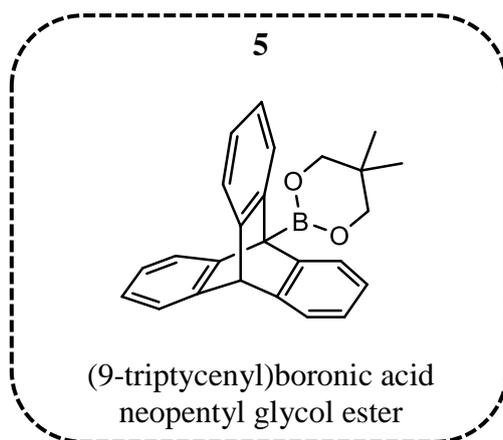
**Temperature** : Room temperature (283-303K)

Table 2 – Atom coordinates for the X-ray structure of compound 3.

Atom label	X (Å)	Y (Å)	Z (Å)
C1	11.001	0.205	11.938
C2	11.041	0.834	11.026
H2	10.410	1.516	11.065
C3	12.034	0.852	10.050
H3	12.067	1.553	9.439
C4	12.965	0.156	9.980
H4	13.634	0.125	9.335
C5	12.912	-1.216	10.865
H5	13.532	-1.906	10.806
C6	11.929	-1.243	11.840
C7	11.735	-2.325	12.886
H7	12.382	-3.057	12.802
C8	9.358	-1.760	12.880
C9	8.008	-2.052	12.810

*Table 2 (Continued) – Atom coordinates for the X-ray structure of compound 3.*

<b>Atom label</b>	<b>X (Å)</b>	<b>Y (Å)</b>	<b>Z (Å)</b>
<b>H9</b>	7.377	-1.373	12.882
<b>C10</b>	7.602	-3.372	12.631
<b>H10</b>	6.695	-3.574	12.592
<b>C11</b>	8.527	-4.379	12.511
<b>H11</b>	8.243	-5.255	12.385
<b>C12</b>	9.882	-4.096	12.577
<b>H12</b>	10.508	-4.780	12.497
<b>C13</b>	10.296	-2.791	12.763
<b>C14</b>	10.902	0.569	14.350
<b>C15</b>	10.232	0.842	15.638
<b>H15</b>	11.716	0.164	16.561
<b>C16</b>	11.681	0.317	17.356
<b>H16</b>	12.632	-1.182	16.422
<b>C17</b>	13.219	-1.373	17.117
<b>H17</b>	12.686	-1.923	15.251
<b>C18</b>	13.296	-2.619	15.160
<b>H18</b>	11.820	-1.613	14.222
<b>C19</b>	10.000	0.368	13.108
<b>C20</b>	9.014	0.864	13.277
<b>B1</b>	7.646	0.789	13.358
<b>O1A</b>	9.446	2.144	13.399
<b>O2A</b>	7.135	2.090	13.765
<b>C21A</b>	8.289	3.040	13.396
<b>C22A</b>	6.867	1.987	15.255
<b>C23A</b>	6.239	1.279	15.419
<b>H23A</b>	6.502	2.817	15.572
<b>H23B</b>	7.688	1.801	15.716
<b>H23C</b>	5.840	2.357	13.003
<b>C24A</b>	6.000	2.270	12.060
<b>H24A</b>	5.533	3.246	13.195
<b>H24B</b>	5.173	1.723	13.274
<b>H24C</b>	8.516	4.159	14.421
<b>C25A</b>	8.665	3.775	15.288
<b>H25A</b>	7.742	4.727	14.452
<b>H25B</b>	9.283	4.678	14.165
<b>H25C</b>	8.178	3.591	11.992
<b>C26A</b>	8.987	4.055	11.765
<b>H26A</b>	7.437	4.200	11.945
<b>H26B</b>	8.039	2.870	11.374
<b>H26C</b>	10.232	0.842	15.638



**Chemical formula :** C<sub>25</sub>H<sub>23</sub>BO<sub>2</sub>

**Molecular weight :** 366.27 g.mol<sup>-1</sup>

In a 50 mL Schlenk flask was added atmosphere 9-bromotriptycene (248 mg, 0.745 mmol, 1.0 eq) in suspension in dry Et<sub>2</sub>O (15 mL). The flask is cooled to -94° with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (0.35 mL, 2.5 M in hexanes, 0.88 mmol, 1.2 eq) was added dropwise under vigorous stirring. 10 min after addition, the bath is removed to allow the reaction to warm up at r.t. and the reaction is stirred for an additional hour. The reaction mixture is then cooled again to -94°C and bis(neopentylglycolato)diboron (253 mg, 1.12 mmol, 1.5 eq) is added. 10 min after addition, the bath is removed and the flask is equipped with a refrigerant after what the mixture is warmed to 40°C and stirred for 4h. The reaction is quenched with water (10 mL). The aqueous layer is extracted with Et<sub>2</sub>O (3x10 mL) and the combined organic layers are dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product is dissolved in CH<sub>2</sub>Cl<sub>2</sub> and precipitation by adding Et<sub>2</sub>O is performed affording the pure product after filtration as a white powder (63 mg, 23%). Crystals suitable for X-ray structure analysis have been obtained by slow evaporation of a saturated solution of **5** in EtOAc.

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 7.73-7.71 (m, 3H), 7.36-7.34 (m, 3H), 6.97-6.95 (m, 6H), 5.33 (s, 1H), 4.07 (s, 4H), 1.29 (s, 6H).

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 147.3, 147.1, 125.2, 124.8, 124.8, 123.5, 72.3, 55.2, 31.93, 22.4 .

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 30.0 .

## X-ray structure of compound 5

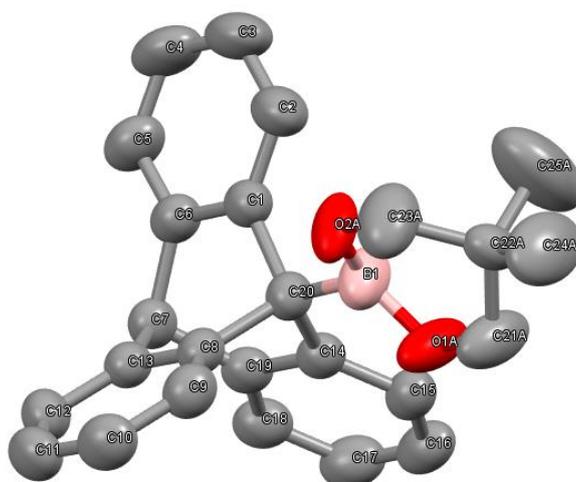


Figure 58 – X-ray structure of compound 5.

**Crystal system** : Monoclinic

**Space group** : P 2<sub>1</sub>/c

**a** : 8.36250(10)      **b** : 20.1714(2)      **c** : 12.32750(10)

**α** : 90°      **β** : 107.3600(10)°      **γ** : 90°

**V** : 1984.72 Å<sup>3</sup>

**Z** : 4

**R-Factor** : 5.01%

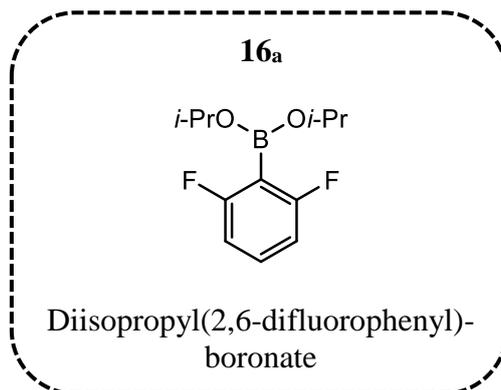
**Temperature** : Room temperature (283-303K)

Table 3 – Atom coordinates for the X-ray structure of 5.

Atom label	X (Å)	Y (Å)	Z (Å)
C1	2.752	7.781	7.207
C2	1.438	7.951	6.814
H2	0.753	7.904	7.441
C3	1.145	8.192	5.482
H3	0.261	8.316	5.221
C4	2.136	8.249	4.544
H4	1.923	8.404	3.652
C5	3.460	8.077	4.918
H5	4.137	8.112	4.282
C6	3.760	7.852	6.248
C7	5.154	7.720	6.833
H7	5.858	7.772	6.153

*Table 3 (Continued) – Atom coordinates for the X-ray structure of compound 5.*

<b>Atom label</b>	<b>X (Å)</b>	<b>Y (Å)</b>	<b>Z (Å)</b>
<b>C8</b>	4.193	6.347	8.594
<b>C9</b>	4.167	5.246	9.432
<b>H9</b>	3.518	5.181	10.095
<b>C10</b>	5.108	4.242	9.284
<b>H10</b>	5.090	3.508	9.855
<b>C11</b>	6.066	4.315	8.308
<b>H11</b>	6.685	3.628	8.211
<b>C12</b>	6.111	5.414	7.466
<b>H12</b>	6.763	5.469	6.805
<b>C13</b>	5.187	6.424	7.614
<b>C14</b>	4.256	8.759	8.854
<b>C15</b>	4.243	9.711	9.860
<b>H15</b>	3.579	9.694	10.510
<b>C16</b>	5.230	10.692	9.891
<b>H16</b>	5.222	11.331	10.567
<b>C17</b>	6.217	10.726	8.935
<b>H17</b>	6.873	11.385	8.969
<b>C18</b>	6.238	9.787	7.924
<b>H18</b>	6.907	9.809	7.278
<b>C19</b>	5.262	8.817	7.880
<b>C20</b>	3.267	7.583	8.653
<b>B1</b>	2.118	7.355	9.727
<b>O1A</b>	2.331	7.683	11.028
<b>O2A</b>	1.290	6.322	9.539
<b>C21A</b>	1.408	7.330	12.064
<b>H21A</b>	1.276	8.100	12.639
<b>H21B</b>	1.802	6.625	12.603
<b>C22A</b>	0.110	6.878	11.581
<b>C23A</b>	0.352	5.832	10.556
<b>H23A</b>	0.717	5.039	10.981
<b>H23B</b>	0.488	5.588	10.135
<b>C24A</b>	0.748	6.326	12.691
<b>H24A</b>	-1.605	6.076	12.338
<b>H24B</b>	0.864	6.995	13.369
<b>H24C</b>	0.321	5.555	13.071
<b>C25A</b>	0.653	8.050	10.902
<b>H25A</b>	-1.539	7.763	10.669
<b>H25B</b>	0.185	8.321	10.109
<b>H25C</b>	0.707	8.792	11.510



**Chemical formula :** C<sub>12</sub>H<sub>17</sub>BF<sub>2</sub>O<sub>2</sub>

**Molecular weight :** 242.07 g.mol<sup>-1</sup>

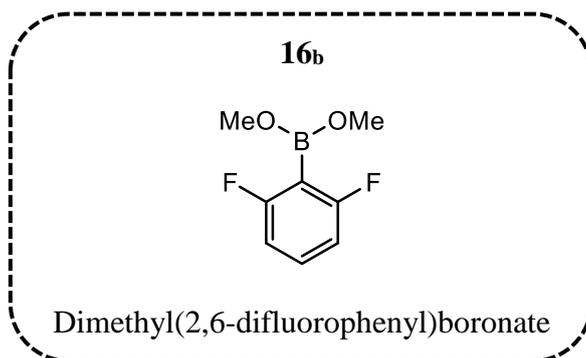
In a 250 mL Schlenk flask was added 1-bromo-2,6-difluorobenzene (6.4 mL, 34 mmol, 1.0 eq) in dry Et<sub>2</sub>O (100 mL). The flask was cooled to -94°C with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (14.5 mL, 2.5 M in hexanes, 36 mmol, 1.1 eq) was added dropwise under vigorous stirring after what the reaction was stirred for 1h45. Triisopropyl borate (7.9 mL, 34 mmol, 1.0 eq) was added dropwise and the reaction is stirred for 2h30. The flask was then warmed to -5°C with an ice/NaCl bath and trimethylsilyl chloride (4.3 mL, 34 mmol, 1.0 eq) was added dropwise after what the bath was removed to allow the reaction to warm to room temperature overnight. Solvents were removed under reduced pressure and a distillation (2 mbar, 100°C) was performed affording the pure product as a colorless liquid (4.5 g, 55%).

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 7.35-7.22 (m, 1H), 6.88-6.79 (m, 2H), 4.44-4.32 (m, 2H), 1.21 (d, *J* = 6.2 Hz, 12H) .

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 164.42 (dd, *J* = 243.3, 14.8 Hz), 131.22 (t, *J* = 9.9 Hz), 111.1-110.8 (m), 66.7, 24.6 .

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 26.0 .

**<sup>19</sup>F NMR (377 MHz, chloroform-*d*) :** δ(ppm) = -103.2 .



**Chemical formula :** C<sub>8</sub>H<sub>9</sub>BF<sub>2</sub>O<sub>2</sub>

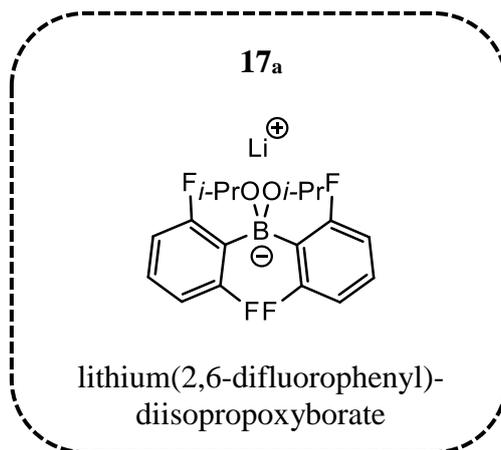
**Molecular weight :** 185.96 g.mol<sup>-1</sup>

In a 100 mL Schlenk flask was added 1-bromo-2,6-difluorobenzene (2.45 mL, 19.9 mmol, 1.0 eq) in dry THF (40 mL). The flask was cooled to -94°C with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (8.4 mL, 2.5 M in hexanes, 21 mmol, 1.1 eq) was added dropwise under vigorous stirring over a period of 15 min after what the reaction was stirred for 1h30. Trimethyl borate (2.26 mL, 19.9 mmol, 1.0 eq) was added dropwise and the reaction was stirred for 1h. The flask was then warmed to -5°C with an ice/NaCl bath and trimethylsilyl chloride (2.6 mL, 1.0 eq) was added dropwise after what the bath was removed to allow the reaction to warm at r.t. overnight. Solvents were removed under reduced pressure and a distillation (8 mbar, 100°C) was performed affording the pure product as a colorless liquid (2.34 g, 64%).

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 7.39-7.27 (m, 1H), 6.90-6.83 (m, 2H), 3.68 (s, 6H).

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 27.2 .

**<sup>19</sup>F NMR (377 MHz, chloroform-*d*) :** δ(ppm) = -102.9 .



**Chemical formula :** C<sub>18</sub>H<sub>20</sub>BF<sub>4</sub>LiO<sub>2</sub>

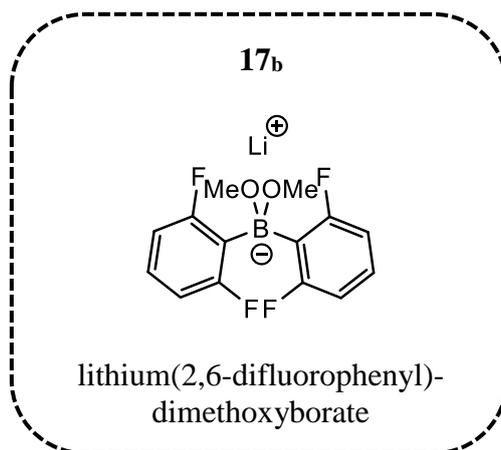
**Molecular weight :** 362.10 g.mol<sup>-1</sup>

In a 100 mL Schlenk flask was added under argon atmosphere 1-bromo-2,6-difluorobenzene (1.24 mL, 9.89 mmol, 1.0 eq) in dry THF (30 mL). The flask was cooled to -94°C with an acetone/N<sub>2(l)</sub> bath and *n*-butyllithium (4.0 mL, 2.5 M in hexanes, 10 mmol, 1.0 eq) was added dropwise under vigorous stirring over a period of 5 min after what the reaction was stirred for 1h45. Compound **16a** (2.24 g, 10.4 mmol, 1.0 eq) in THF (3 mL) was added dropwise and the reaction was stirred for an additional 2h at -94°C after what the bath is allowed to reach r.t. overnight. Solvents were removed under reduced pressure. The residue is washed with CH<sub>2</sub>Cl<sub>2</sub> affording the pure product as a white powder (2.32 g, 67%).

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 6.89-6.79 (m, 2H), 6.47-6.38 (m, 4H), 4.34 (s, 2H), 0.77 (dd, *J* = 6.0, 2.1 Hz, 6H).

**<sup>11</sup>B NMR (160 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 1.4 .

**<sup>19</sup>F NMR (377 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = -98.6 .



**Chemical formula :** C<sub>14</sub>H<sub>12</sub>BF<sub>4</sub>LiO<sub>2</sub>

**Molecular weight :** 305.99 g.mol<sup>-1</sup>

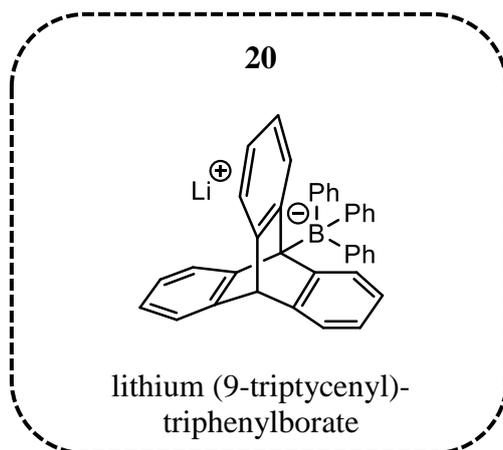
In a 100 mL Schlenk flask was added under argon atmosphere 1-bromo-2,6-difluorobenzene (0.62 mL, 5.0 mmol, 1.0 eq) in dry THF (15 mL). The flask was cooled to -94°C with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (2.1 mL, 2.5 M in hexanes, 5.3 mmol, 1.1 eq) was added dropwise under vigorous stirring over a period of 5 min after what the reaction was stirred for 1h45. Compound **16b** (966 mg, 4.68 mmol, 0.94 eq) in THF (10 mL) was added dropwise and the reaction was stirred for an additional 2h at -94°C after what the bath was allowed to reach room temperature overnight. A filtration was performed affording the pure product as a white powder (1.01 g, 69%).

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 6.94-6.84 (m, 2H), 6.52-6.44 (m, 4H), 2.91 (s, 6H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 167.7 (d, *J* = 20.1 Hz), 165.3 (d, *J* = 19.8 Hz),, 125.5 (t, *J* = 10.8 Hz), 109.9, 109.5, 104.0, 49.0 .

**<sup>11</sup>B NMR (160 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 2.4 .

**<sup>19</sup>F NMR (377 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = -100.3 .



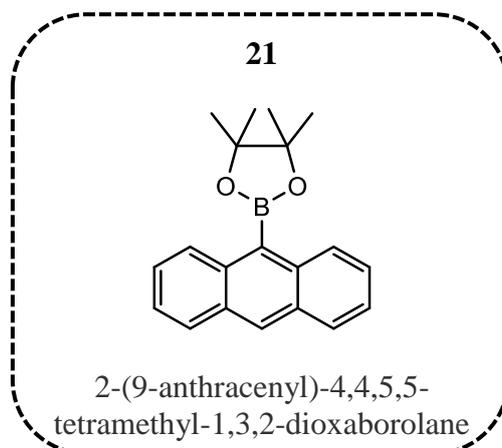
**Chemical formula :** C<sub>38</sub>H<sub>28</sub>BLi

**Molecular weight :** 502.39 g.mol<sup>-1</sup>

In a 100 mL Schlenk flask was added 9-bromotriptycene (200 mg, 0.60 mmol, 1.0 eq) in dry Et<sub>2</sub>O (20 mL). The flask is cooled to -94°C with an acetone/N<sub>2(l)</sub> bath and *n*-butyllithium (0.29 mL, 2.5 M in hexanes, 0.73 mmol, 1.2 eq) was added dropwise under vigorous stirring. 10 min after addition, the bath is removed to allow the reaction mixture to warm up at r.t. and the reaction is stirred for 50 min. The reaction mixture is then cooled again to -94°C and triphenyl borane (200 mg, 0.90 mmol, 1.5 eq) dissolved in dry Et<sub>2</sub>O (5 mL) is added under stirring. 10 min after addition, the reaction is allowed to warm at room temperature over a period of 1h and then warmed to 40°C and stirred overnight. Then a filtration under argon atmosphere is performed and the precipitate is washed with Et<sub>2</sub>O (4x5 mL) affording the pure product as a white powder (172 mg, 57%).

**<sup>1</sup>H NMR (400 MHz, acetonitrile-*d*<sub>3</sub>) :** δ(ppm) = 7.35-7.27 (m, 9H), 7.25 (d, *J* = 7.8 Hz, 3H), 6.89-6.82 (m, 9H), 6.77 (td, *J* = 7.3, 1.1 Hz, 3H), 6.43-6.35 (m, 3H) , 5.38 (s, 1H).

**<sup>11</sup>B NMR (160 MHz, acetonitrile-*d*<sub>3</sub>) :** δ(ppm) = -9



**Chemical formula :** C<sub>20</sub>H<sub>21</sub>BO<sub>2</sub>

**Molecular weight :** 304.20 g.mol<sup>-1</sup>

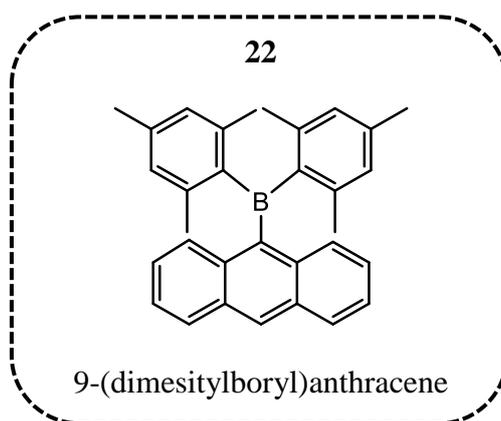
Prepared according to a modified literature procedure.<sup>(2)</sup> In a 100 mL Schlenk flask was added 9-bromoanthracene (2.00 g, 7.78 mmol, 1.0 eq) in dry Et<sub>2</sub>O (25 mL). The flask is cooled to -78°C with an acetone/CO<sub>2(s)</sub> bath and *n*-butyllithium (3.8 mL, 2.5 M in hexanes, 8.3 mmol, 1.1 eq) was added dropwise under vigorous stirring. 10 min after addition, the reaction is warmed to 0°C thanks to an ice bath and stirred for 50 min. The reaction mixture is then cooled again to -78°C and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.4 mL, 7.1 mmol, 1.1 eq) is added under stirring. 10 min after addition, the reaction is allowed to warm at room temperature and stirred overnight. The reaction is quenched with water (20 mL). The aqueous layer is extracted with EtOAc (3x20 mL) and the combined organic layers are dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude product is purified by flash chromatography using cyclohexane/EtOAc (80:20) as an eluant affording the pure product (1.16 g, 49%). NMR data were in agreement with the literature.

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 8.49 (s, 1H), 8.46 (d, *J* = 8.7 Hz, 2H), 8.00 (dd, *J* = 8.3, 0.7 Hz, 2H), 7.53-7.43 (m, 4H), 1.59 (s, 12H).

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 136.0, 131.3, 129.6, 128.9, 128.4, 125.9, 125.0, 84.5, 25.3 .

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 32.2 .

<sup>(2)</sup> S. Ye, J. Chen, C.-A. Di, Y. Liu, K. Lu, W. Wu, C. Du, Y. Liu, Z. Shuai, G. Yu, *J. Mater. Chem.*, **2010**, 20, 3186-3194.



**Chemical formula :** C<sub>32</sub>H<sub>31</sub>B

**Molecular weight :** 426.41 g.mol<sup>-1</sup>

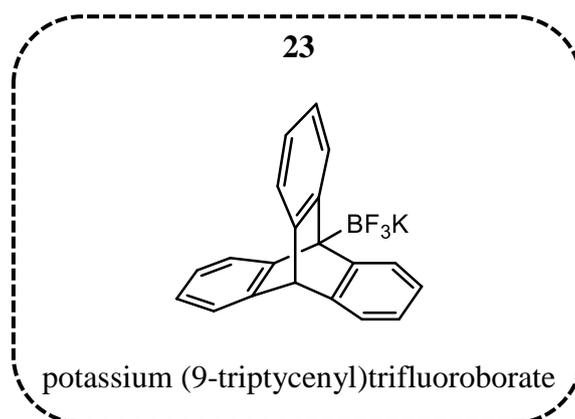
Prepared according to a modified literature procedure.<sup>(3)</sup> In a 100 mL Schlenk flask was added 9-bromoanthracene (1.67 g, 6.48 mmol, 1.0 eq) in dry Et<sub>2</sub>O (18 mL). The flask is cooled to -94°C with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (3.1 mL, 2.5 M in hexanes, 7.8 mmol, 1.2 eq) was added dropwise under vigorous stirring. 10 min after addition, the reaction is warmed to 0°C thanks to an ice bath and stirred for 45 min. The reaction mixture is then cooled again to -94°C and dimesitylboron fluoride (1.91 g, 7.13 mmol, 1.1 eq) dissolved in Et<sub>2</sub>O (10 mL) is added under stirring. 10 min after addition, the reaction is allowed to warm at room temperature and stirred overnight. The crude product is concentrated under reduced pressure and then dissolved in CH<sub>2</sub>Cl<sub>2</sub> and then filtered. The filtrate is evaporated and the residue is extracted in hot EtOAc affording the pure product after filtration (1.51g, 54%). <sup>1</sup>H NMR data were in agreement with the literature.

**<sup>1</sup>H NMR (400 MHz, chloroform-*d*) :** δ(ppm) = 8.49 (s, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.40-7.35 (m, 2H), 7.25-7.19 (m, 2H), 6.88 (br, 2H), 6.65 (br, 2H), 2.28 (s, 6H), 2.18 (br, 6H), 1.62 (br, 6H).

**<sup>13</sup>C NMR (100 MHz, chloroform-*d*) :** δ(ppm) = 146.0, 145.7, 140.8, 139.8, 134.1, 131.3, 129.8, 129.2, 129.1, 128.5, 125.4, 125.0, 23.5, 21.5 .

**<sup>11</sup>B NMR (160 MHz, chloroform-*d*) :** δ(ppm) = 80.8 .

<sup>(3)</sup> J.F. Blount, P. Finocchiaro, D. Gust, K. Mislow, K., *J. Am. Chem. Soc.* **1973**, 95, 7019–7029.



**Chemical formula :** C<sub>20</sub>H<sub>13</sub>BF<sub>3</sub>K

**Molecular weight :** 360.63 g.mol<sup>-1</sup>

In a 500 mL Schlenk flask was added 9-bromotriptycene (5.06 g, 15.18 mmol, 1.0 eq) in dry Et<sub>2</sub>O (250 mL). The flask was cooled to -94°C with an acetone/N<sub>2</sub>(l) bath and *n*-butyllithium (6.6 mL, 2.5 M in hexanes, 17 mmol, 1.1 eq) was added dropwise under vigorous stirring. 10 min after addition, the bath was removed to allow the reaction mixture to warm up for a period of 1h. The reaction mixture was then cooled again to -94°C and tributyl borate (6.0 mL, 22 mmol, 1.5 eq) was added under stirring. 10 min after addition, the reaction is warmed to 40°C and stirred overnight. Then the flask is cooled to 0°C thanks to an ice bath and potassium hydrogenfluoride (7.03 g, 90.0 mmol, 5.9 eq) in water (50 mL) was added dropwise and the reaction is stirred for 1h at 0°C and then stirred at r.t. overnight. The solvents were then evaporated under reduced pressure and a filtration with hot acetone was performed. The filtrate was then evaporated until there is only few mL of acetone in the flask left and a precipitation was performed by adding Et<sub>2</sub>O. Then a filtration afforded the pure product as a white powder (2.13 g, 39 %).

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 7.69 (d, *J* = 6.7 Hz, 3H), 7.24 (dd, *J* = 6.4, 1.8 Hz, 3H), 6.81 (m, 6H), 5.30 (s, 1H).

**<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 150.6, 148.8, 126.9, 123.5, 122.9, 122.4, 54.27.

**<sup>11</sup>B NMR (160 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = 3.9 .

**<sup>19</sup>F NMR (377 MHz, DMSO-*d*<sub>6</sub>) :** δ(ppm) = -135.2 .

## **6. REFERENCES**

- [1] G.N. Lewis. *Valence and the Structure of Atoms and Molecules*. Chemical Catalog Com, New York, **1923**.
- [2] D.R. Lide, *CRC handbook of chemistry and physics*. CRC, Boca Raton, **2012**.
- [3] I.B. Sivaev, V.I. Bregadze, *Coord. Chem. Rev.* **2014**, 270, 75-88.
- [4] E.M. Rothe, B.P. Mathur, G.P. Reck, *Inorg. Chem.* **1980**, 19, 829-831.
- [5] J.A. Nicasio, S. Steinberg, B. Ines, M. Alcarazo, *Chem. Eur. J.* **2013**, 19, 11016–11020.
- [6] P.A. Chase, W.E. Piers, B.O. Patrick, *J. Am. Chem. Soc.* **2000**, 122, 12911–12912.
- [7] P.A. Chase, P.E. Romero, W.E. Piers, M. Parvez, B.O. Patrick, *Can. J. Chem.* **2005**, 83, 2098–2105.
- [8] R. S. Mulliken, *J. Phys. Chem.* **1952**, 56, 801-822.
- [9] K.O. Christe, D.A. Dixon, D. McLemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, *J. Fluorine Chem.* **2000**, 101, 151–153.
- [10] M.A. Beckett, G.C. Strickland, J.R. Holland, K.S. Varma, *Polym. Commun.* **1996**, 37 4629–4631.
- [11] R.F. Childs, D.L. Mulholland, A. Nixon, *Can. J. Chem.* **1982**, 60, 801–808.
- [12] T.W. Graham Solomons, C.B. Fryhle, *Organic Chemistry*, Wiley, New York, **2002**.
- [13] R. Anulewicz-Ostrowska, S. Luliński, E. Pindelska J. Serwatowski, *Inorg. Chem.* **2002**, 41, 2525-2528.
- [14] V.H. Dodson, W.E. Fisher, *OJS* **1958**, 58, 141-144.
- [15] H.C. Brown, V.H. Dodson, *J. Am. Chem. Soc.* **1957**, 79, 2302-2306.
- [16] H. Yamamoto, *Lewis Acids in Organic Synthesis*, Wiley-VCH, New York, **2000**.
- [17] K. Ishihara, N. Hanaki, H. Yamamoto, *Synlett* **1993**, 577.
- [18] W.E. Piers, T. Chivers, *Chem. Soc. Rev.*, **1997**, 26, 345-354.
- [19] Z. Chen, K. Amine, *J. Electrochem. Soc.* **2009**, 156, A672-A676.
- [20] S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2001**, 123, 11372-11375.
- [21] D.W. Stephan, *Org. Biomol. Chem.* **2008**, 6, 1535-1539.
- [22] G.C. Welch, R.R.S. Juan, J.D. Masuda, D.W. Stephan, *Science* **2006**, 314, 1124.
- [23] L. Zhao, Z. Li, T. Wirth, *Chem. Lett.* **2010**, 39, 658-667.
- [24] F.K-C. Leung, F. Ishiwari, Y. Shoji, T. Nishikawa, R. Takeda, Y. Nagata, M. Suginome, Y. Uozumi, Y.M.A. Yamada, T. Fukushima, *ACS Omega.* **2017**, 2, 1930-1937.

- [25] D.K. Frantz, K.K. Baldrige, J.S. Siegel, *CHIMIA* **2009**, 63, 201-204.
- [26] Y. Jiang & C.F. Chen, *Eur. J. Org. Chem.* **2011**, 2011, 6377-6403.
- [27] J.B. Baruah, *Concepts for Molecular Machines*. World Scientific, New Jersey, **2017**.
- [28] T.R. Kelly, H. De Silva, R.A. Silva, *Nature* **1999**, 401, 150.
- [29] C.E. Godinez, G. Zepeda, M.A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, 124, 4701-4707.
- [30] I.K. Mati, S.L. Cockroft, *Chem. Soc. Rev.* **2010**, 39, 4195-4205.
- [31] B.W. Gung, X. Xue, H.J. Reich, *J. Org. Chem.* **2005**, 70, 3641-3644.
- [32] D.H. Busch, *Chem. Rev.* **1993**, 93, 847.
- [33] O. Grossman, C. Azerraf, D. Gelman, *Organometallics* **2006**, 25, 375-381.
- [34] G. Wittig, W. Tochtermann, *Justus Liebigs Ann. Chem.* **1962**, 660, 23-33.
- [35] R.J. Baker, *J. Organomet. Chem.* **2004**, 689, 781-790.
- [36] C-H Chen, F.P. Gabbai, *Chem. Sci.* **2018**, 9, 6210-6218.
- [37] Y. Kawada & H. Iwamura, *J. Am. Chem. Soc.* **1983**, 105, 1449-1459.
- [38] Y. Kawada & H. Iwamura, *J. Am. Chem. Soc.* **1981**, 103, 958-960.
- [39] T. Okuyama, H. Maskill, *Organic chemistry: a mechanistic approach*. Oxford University Press, **2013**.
- [40] K.P. Kepp, *Inorg. Chem.* **2016**, 55, 9461-9470.
- [41] S.Y. Arkhipenko, *Approaches to Novel B-N Chemistry at the Boundary of Frustrated Lewis Pairs and Bifunctional Catalysis*, Durham theses, Durham University, **2017**.
- [42] K. Peters, E.-M. Peters, T. Panitzsch, W. Tochtermann, *Z. Kristallogr. - New Cryst. Struct.* **1999**, 214, 89-90.
- [43] J. Chmiel, I. Heesemann, A. Mix, B. Neumann, H.G. Stammler, M.W. Mitzel, *Eur. J. Org. Chem.* **2010**, 2010, 3897-3907.