Boron-based donor-spiro-acceptor compounds as novel thermally activated delayed fluorescence (TADF) emitters

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To my parents, Carla and Giuseppe.
Abstract

Thermally activated delayed fluorescence (TADF) emitters played a pivotal role in the improvement of organic light-emitting diode (OLED) technology. Thanks to the participation of triplet excited states in the delayed emission, diodes based on TADF chromophores display high efficiencies comparable to those of diodes that make use of transition metal-based phosphorescent emitters. In addition, employing purely organic emitters presents additional advantages connected to the cost of the emitters and their environmental impact.

The molecular architecture of purely organic TADF emitters is directly connected to the observation and efficiency of the delayed emission. In particular, adopting a donor-acceptor architecture where the two different fragments are tilted, one with respect to the other, has proven to be an efficient strategy for designing efficient TADF emitters. A way to guarantee this spatial disposition is introducing a spiro center between the donor and acceptor fragments, which forces the two moieties in an orthogonal arrangement. This thesis discusses the synthesis of two different classes of donor-spiro-acceptor compounds, which both include a boron atom in the molecular structure but at different positions and with a coordinations.

The first part of the thesis discusses the synthesis and functionalization of emitters that contain a tetracoordinated boron atom as the spiro center. The investigated acceptor fragments were based on the phenylpyridine moiety, whereas the donors employed were based on a disulfide, di- or triarylamine fragment. By combining different donors and acceptors, nine different emitters were synthesized and analyzed, which allowed us to establish a correlation between the emission wavelength and the relative strength of the two fragments. Additionally, the characterization of the photophysical properties of these emitters showed that the adopted molecular architecture successfully induced the emission via thermally delayed fluorescence in most cases. Nonetheless, the emitters belonging to this class displayed a low quantum yield in solution, which could be caused by the relatively high flexibility of the donor moieties employed. Therefore, an improvement of the chromophores’ performances can be potentially obtained by implementing a more rigid donor fragment in the molecular structure. Additionally, it was shown how the derivatization of the emitters’ donor moiety can be used to synthesize different chiral emitters or to insert a transition metal center in the molecular structure, thereby expanding the potential applications of this class of compounds.

The second part of the thesis discusses the development of a synthesis path toward a class of emitters in which structure the boron atom is tricoordinated and confers the electron-accepting nature to the 9-bora-9,10-dihydroanthracene-based acceptor fragment. In this class of compounds, the spiro center is constituted by a carbon atom and the donor fragment by a triphenylamine moiety. The developed synthesis path was designed with the aim of generating a common precursor which photophysical properties could be tuned by exchanging the third substituent at the tricoordinated boron center. With the developed synthesis pathway, the derivative with a 9-mesityl-9-bora-9,10-dihydroanthracene acceptor moiety was synthesized and the analysis of its photophysical properties confirmed the emission via TADF and, consequently, the potential of this class of compounds.

The emission via TADF involves relatively long-lived triplet excited states, making TADF chromophores also potentially applicable in photocatalysis. To investigate the performance of the synthesized emitters in this field, one compound from each of the above-mentioned classes was tested in photosensitized and photoredox reactions. The outcome of the catalytic trial showed that both tested compounds do promote photosensitized reactions via the generation of singlet oxygen. However, the two chromophores did not display photocatalytic activity in any of the tested photoredox transformations.
Zusammenfassung


Der erste Teil der Dissertation befasst sich mit der Synthese und Funktionalisierung von Emittern, bei denen sich das Boratom an dem Spirozentrum befindet und daher vierfach koordiniert ist. Die untersuchten Akzeptor-Fragmente basierten auf der Phenylpyridin-Einheit, während die eingesetzten Donoren auf einem Disulfid-, Di- oder Triarylamino-Fragment basierten. Durch die Kombination verschiedener Donoren und Akzeptoren konnten 9 unterschiedliche Emitter synthetisiert werden, was uns erlaubte, einen Zusammenhang zwischen der Emissionswellenlänge und der relativen Stärke der beiden Fragmenten herzustellen. Darüber hinaus zeigte die Charakterisierung der photophysikalischen Eigenschaften dieser Emitter, dass die gewählte molekulare Architektur in den meisten Fällen erfolgreich die Emission über thermisch verzögerte Fluoreszenz induziert. Dennoch zeigten die zu dieser Klasse gehörenden Emitter in Lösung eine geringe Quantenausbeute, was durch die relativ flexiblen Donoreinheiten induziert werden könnte. Daher kann möglicherweise eine Verbesserung ihrer Leistungen durch die Implementierung eines starreren Donorfragments in die Molekülstruktur erreicht werden. Außerdem konnte gezeigt werden, wie die Derivatisierung der Donoreinheit der Chromophore potenziell genutzt werden kann, um verschiedene chirale Emitter zu synthetisieren oder ein Übergangsmetallzentrum in die Molekülstruktur einzufügen, was die Anwendungsmöglichkeiten dieser Verbindungsklasse immens erweitert.


Die Emission über TADF beinhaltet relativ langlebige angeregte Tripletzustände, wodurch TADF-Chromophore auch in der Photokatalyse eingesetzt werden könnten. Um die Leistungsfähigkeit der
Drawings and naming conventions

A summary of the chromophores synthesized in this work whose photophysical properties have been characterized is attached at the hard cover of this thesis. In all the structures reported in this work, the coordinative bond between a boron and a nitrogen atom is depicted with the same style as the other covalent bonds, and the formal charges are omitted for clarity. The names of the compounds are identified with a number that follows the order of appearance in the text. The prefixes En- or Di- before the compound number indicate that the mixture of enantiomers or diastereomer is considered, respectively. The stereo descriptors, R or S, reported before the compound name, are used to indicate only one of the possible enantiomers.
Abbreviation list

CD  circular dichroism
CT  charge-transfer or charge transfer excited state
DCE  dichloroethane
DCM  dichloromethane
DDQ  2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMEA  dimethyl Dimethylethanolamine
DMSO  dimethyl sulfoxide
'Pr  isopropyl
ISC  intersystem crossing
LE  Locally-excited state
LiDBB  lithium 4,4'-Di-tert-butylbiphenylide
Mes  Mesitylene
Mg\textsuperscript{a}  magnesium powder generated by the decomposition of the complex Mg(anthracene)∙3THF under vacuum
Mg\textsuperscript{a}  Rieke magnesium
NBS  N-bromosuccinimide
'\textup{Bu}  normal butyl
NCS  N-chlorosuccinimide
PET  photo-electron-transfer
PLQY  photoluminescence quantum yield
PMMA  polymethyl methacrylate
r.t.  room temperature
R\textsubscript{f}  retention factor (TLC)
rISC  reverse intersystem crossing
RTP  room temperature phosphorescence
TADF  thermally activated delay fluorescence
'\textup{Bu}  tert-butyl
TCSPC  Time-correlated single photon counting
Tf  trifluoromethylsulfonyl
THF  tetrahydrofuran
TMEDA  N\textsubscript{1}, N\textsubscript{1}, N\textsubscript{2}, N\textsubscript{2}-tetramethylethane1,2-diamine
TMS-Cl  Trimethylsilyl chloride
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1. Introduction

Displays have become essential devices in our everyday lives and are the key interface between us and the digital world. Comparing one of the first commercialized televisions with one of the displays available on the market today gives a clear measure of the extraordinary technological progress that has taken place in the field of display devices in a period of about 100 years. Not only did technological advancements allow to drastically improve the quality of the displayed image but they also permitted the construction of devices with remarkable design characteristics, from screens with a reduced thickness of 4 mm to foldable or even transparent displays. These transformations were enabled by the invention of solid-state lighting technologies, namely light-emitting-diodes (LEDs), and their successors the organic light-emitting diodes (OLEDs), which are based on organic emitters. The combination of LED with liquid crystal display (LCD) led to displays with a drastically reduced weight and thickness compared to standard cathode-ray tubes (CRT). However, it was the invention of OLEDs that allowed to truly break the boundaries of design and applications.

The diffusion of OLEDs-based displays is increasing, especially thanks to its application in mobile devices, such as smartphones or consoles. Lighting devices based on OLED are less widespread and are generally found in all instances where particular design requirements do not allow the use of the more rigid LEDs. OLEDs are still a relatively young technology compared to LED, and in some applications, LEDs still are the best option. In particular, LEDs are usually superior to OLEDs in terms of production cost, device longevity and maximal luminosity of the diode. For these reasons, the two technologies are parallelly employed and chosen based on the requirements of the applications.

As can be understood from the above, OLED technology is at its early development stage and the active object of research that aims to solve the illustrated downsides, close the gap with LEDs, and eventually deliver a better alternative. A fundamental component of these devices is clearly the emissive organic material employed. As illustrated in the next chapters, the change in the kind of chromophore used in the emissive layer marked some of the most distinct milestones in the development of OLEDs. Improving the photophysical and chemical properties of the emitter constitute one of the most direct approaches to improve the device lifetime, efficiency, and brightness. Therefore, the development of new emitters has engaged chemists since the early development stages of this technology and is also the object of the present work. Before describing the operating principle and evolution of the OLED technology, it is worth summarizing the key concepts behind molecular luminescence and introducing the family of emitters that are the main object of this thesis.

1.1. Molecular luminescence

Luminescence is defined as "a spontaneous emission of radiation from an electronically excited species not in thermal equilibrium with its environment."¹ This definition includes different phenomena that can be differentiated on the basis of the process responsible for the excitation of the emitters. In OLEDs, luminescence is generated by an electronically excited organic chromophore generated upon application of an electric voltage. For this reason, the emission of these devices is described as electroluminescence. A molecule in an electronically excited state does not only undergo relaxation vai
radiative deactivation but can also participate in non-radiative deactivation processes. The main characteristics of both kinds of pathways are summarized in the following sections.

1.1.1. Selection rules

An electronically excited molecule can undergo different monomolecular deactivation processes: vibrational relaxation, radiationless, and radiative deactivations. However, the excited state can also participate in deactivation pathways involving bimolecular processes. This macro-category includes, for instance, triplet-triplet annihilation processes, the formation of excimers, or chemical reactions.

The energy diagram, also known as the Perrin-Jablonski diagram (Fig. 1), is a convenient way of graphically summarizing the different monomolecular deactivation pathways in which an electronically excited molecule is involved. The diagram represents the different electronic states in which an excited state molecule can be found and the related vibration levels. Arrows are used to represent the different processes that connect these states. Straight arrows indicate processes that lead to the emission of light, whereas wavy arrows indicate non-radiative processes. The excited states are identified with a letter and a number. The letter indicates their spin multiplicity, S for singlet and T for triplet. The number refers to the relative position of the excited state with respect to the states with the same multiplicity on the energy scale.

![Fig. 1 Perrin–Jablonski diagram. Straight lines correspond to radiative transitions; wavy lines correspond to non-radiative transitions. VR stands for vibrational relaxation, IC stands for internal conversion, ISC stands for intersystem crossing, and rISC stands for reverse intersystem crossing.](image)

The electronic transitions’ probability and intensity are related to the transition dipole moment (TM). This parameter is calculated by using the wavefunction of the initial and final state of the transition (Ψᵢ and Ψᵣ). Its factorized and approximated form (Equation 1) is constituted by three different integrals from which the selection rules for a generic transition are derived. This expression is obtained under the Franck-Condon approximation, which states that the movement of the nucleus is negligible in the time of the electronic transition and that during an electronic transition, the geometry of the molecule, hence the position of the nuclei, is not affected. This principle allows to separate the nuclear and electronic wavefunctions, but it cannot always be considered valid. A transition between two given states is considered allowed if TM ≠ 0; hence, none of the three factors should equal zero.
\[ \text{TM} = \int \Psi_i \hat{\mu} \Psi_f d\tau = \int \phi_i \hat{\mu} \phi_f d\tau_e \int S_i S_f d\tau_S \int \theta_i \theta_f d\tau_N \]

Equation 1. Simplified and factorized expression for the transition dipole moment. The wavefunction describing the initial and final state of the transition (\(\Psi_i\) and \(\Psi_f\), respectively) had been factorized in three different components. Namely, the corresponding electronic (\(\phi\)), spin (\(S\)) and nuclear wavefunction (\(\theta\)).

The result of the electronic transition moment integral, \(\int \phi_i \hat{\mu} \phi_f d\tau_e\), is connected to the symmetry of the orbitals involved in the transition. The integral delivers a value different from zero, and therefore refers to an allowed transition, if the function produced by the internal product is not antisymmetric. Another relevant element that influences the result of this integral is the overlap between the orbitals involved in the transitions. A higher spatial overlap between these orbitals translates into a higher value of the electronic transition moment and, therefore, into a higher intensity for the transition.

The integral \(\int S_i S_f d\tau_S\) reflects the effect of the electron spin on the transition dipole moment. The integral delivers a value of 1 if the transition does not involve a change in multiplicity but one of 0 if there is a change in spin multiplicity. It follows that singlet-singlet and triplet-triplet transition are spin allowed, whereas triplet-singlet and singlet tripled transition are spin-forbidden. Singlet-singlet transitions are, in fact, commonly observed since the ground state of most molecules has a singlet multiplicity. This selection rule, however, is strictly valid, if spin and orbital functions can be considered independent. Spin-orbit coupling interaction allows states with different spins to be mixed, permitting transitions between states with different multiplicities. The magnitude of the spin-orbit coupling perturbation is proportional to the fourth power of the atomic number. Therefore, it is generally referred to as the heavy atom effect since it does not affect the vast majority of the organic molecules that do not contain heavy atoms such as transition metals. As illustrated later, under special conditions, transitions between states with different spin multiplicities can also occur without the presence of heavy metal centers.

The last term of the equation, \(\int \theta_i \theta_f d\tau_N\), also known as the Frank-Condon term, represents the overlap between the nuclear wavefunctions. It reflects the Frank-Condon principle at a quantum mechanical level and indicates that the transition probability can be calculated at a fixed nuclear position. It does not lead to the formulation of a selection rule but is directly connected to the bands' shape in the absorption spectrum. The Frank-Condon term indicates that a transition is favored when there is a significant overlap between the vibrational wavefunctions of the initial and final states of the transition. According to this condition, transitions in which the relative positions of the nuclei are the same in the initial and final states are favored.

1.1.2. Vibrational relaxation

This process occurs between vibrational levels of an electronic state. Independently from the excitation source, the electronically excited state can be generated at a high vibrational level. These so-called "hot" species tend to relax to the vibrational ground state via the collision with other molecules of the surrounding environment, which act as a heat sink. In gasses, where the collisions between molecules are less frequent, excited molecules tend to relax to the vibrational ground state via intramolecular vibrational redistribution. Vibrational relaxation is the fastest process in which the electronically excited state can take part. For this reason, it is assumed that the other deactivation processes take place from thermally equilibrated excited states.
1.1.3. **Radiationless deactivation**

This process occurs between isoenergetic vibrational levels of different electronic states. It is referred to as internal conversion (IC) if the initial and final state have the same spin multiplicity or intersystem crossing (ISC) if the multiplicity of the excited state changes between the initial and final state of the transition. These transformations are generally considered irreversible since they are associated with an increase in entropy (higher vibrational level on a lower energy excited state) and because the vibrational relaxation is an extremely fast process that rapidly converts the excited molecule to the vibrational ground state.

According to perturbation theory, the rate constant of the isoenergetic radiationless transitions is given by the Fermi golden rule (Equation 2).

\[
 k_{nr} = \left( \frac{2\pi}{\hbar} \right) \langle \phi_i | \hat{H}' | \phi_f \rangle^2 \sum_n \langle \theta_{i,n} | \theta_{f,n} \rangle^2 
\]

*Equation 2 Rate constant of radiationless transitions expressed in terms of Fermi’s golden rule.*

The operator \( \hat{H}' \) represents an appropriate perturbation that promotes the transition. For IC is indicated with \( \hat{R}_{ic} \) whereas for ISC the operator corresponds to \( \hat{R}_{SO} \), the spin-orbit coupling operator.

In the expression for IC, due to the symmetry requirements of the operator, internal conversion transitions from, for instance, \( S_1 \) to \( S_0 \) should not be allowed. However, this kind of conversion and other not allowed radiationless transitions can still be observed with lower rates due to vibronic coupling. The presence of this coupling connects the electronic and nuclear motion, and, as a result, separating the electronic from the nuclear wave functions as in Equation 1 or Equation 2 is not possible. The reciprocal influence between nuclear vibration and electron motion ultimately removes the symmetry constraints, partially allowing the transition. IC must be particularly taken into account when discussing fluorescence emitters. As for IC, emission via fluorescence involves two states with the same multiplicity, and the radiative transition usually proceeds via the relaxation of an excited molecule from \( S_1 \) to \( S_0 \) (chapter 1.1.4). The fact that both processes may originate from the same excited states renders internal conversion a direct competing process of the radiative emission from \( S_1 \).

The ISC transition and the related selection rules are relevant for the topic discussed in this thesis since the process of thermally activated fluorescence (TADF) is based on the reverse-intersystem crossing (rISC) between a triplet and singlet excited states. As previously mentioned, the magnitude of the spin-orbit coupling is generally low if no heavy atom is present in the molecule or eventually in the environment around the molecule itself. However, thanks to the mechanism that will be later explained, in TADF emitters, the rISC process can occur without the assistance of a heavy atom. From the matrix element \( \langle \phi | \hat{H}_{SO} | \phi \rangle \) it is possible to derive selection rules for the ISC and rISC transitions. In this context, the rules take the name of El-Sayed rules, and they state that an intersystem crossing transition is allowed between excited states of different nature. For instance, the transition \( ^1(n, \pi^*) \leftrightarrow ^3(n, \pi^*) \) is not allowed since both excited states display the same \( n, \pi^* \) character. From a quantum mechanical perspective, resolving the integrals for the two spatial wave functions would deliver zero as the result, thereby leading to a null \( k_{isc} \). Conversely, the transition \( ^1(n, \pi^*) \leftrightarrow ^1(\pi, \pi^*) \) is allowed since the character of the two excited states is different. From a classical point of view, this selection rule indicates that, to satisfy the principle of conservation of angular momentum, a change in the electronic spin angular momentum of the should be
counterbalanced by a change of the orbital angular momentum. In the context of TADF emitters, El-Sayed rules are relevant because the excited states involved in the rISC process formally have the same character. Therefore, for the transition to take place, other conditions must be met as it is later described.

The analysis of the Frank-Condon term in Equation 2 \( \langle \theta_i,0 | \theta_f,n \rangle \) leads to an essential consideration about the rate of radiationless transitions, which finds its exemplification in the energy gap law. This law states that the lower is the energy difference between the two states involved in the transition, the higher is the probability of radiationless transition. This law can be motivated considering that the higher is the energy gap between the two states, the higher is the quantum number associated with the excited vibrational state of the lower state isoenergetic with the vibrational ground state of the higher state. Vibrational wavefunctions with a higher quantum number display a poor overlap with ground-state vibrational wavefunctions, leading to a low value of the Frank-Condon term. For this reason, the probability of a radiationless transition and its rate decrease exponentially with the energy gap between the two states. Considering that the energy difference between higher excited states is lower than the energy difference between the ground state and the first excited state, it follows that, according to the energy-gap law, radiationless transitions between higher excited states are more common than between the first excited state and the ground state. For the same reason, radiative relaxations, as fluorescence, can compete with radiationless transition only for transitions that involve the ground state and the first excited state. Transitions involving higher excites states are instead dominated by radiationless decay processes.

The energy-gap law can be considered valid when the minima of the two nuclear wave functions are nested (Fig. 2a). If the potential energy surfaces of the two states are crossing in the vicinity of the minimum for the higher excited state, the radiationless transition is highly favored and largely independent from the energy gap between the two states (Fig. 2b). The intermediate case between these two limiting cases is of particular interest for thermally activated processes. In this situation, the minimum of the higher excited state is nested, but an intersection between the potential energy surfaces of the two states is not too distant from the excited state minimum. In this case, the most favorable way for the molecule to undergo the radiationless transition may be through the intersection between the two surfaces, requiring a certain thermal excitation.

Fig. 2 Limiting cases for the potential energy surfaces of the nuclear wavefunctions in radiationless transitions, picture extracted form the reported reference.\(^2\) a) nested nuclear wavefunctions b) intersecting potential energy surfaces at the minimum of the excited state’s nuclear wavefunction.
Substitution of the hydrogen atoms in the molecular structure with deuterium influences the vibrational levels' energy of the molecule. The higher mass of deuterium lowers the frequency of oscillation and, therefore, the zero-point energy. According to the energy gap law, this change in energy translates to a reduction overlap between the nuclear wavefunctions of the two states in the deuterated molecule. It follows that deuteration can be used to suppress non-radiative processes in favor of radiative transitions.

1.1.4. Radiative deactivation

The processes that lead to the relaxation of the electronically excited state with light emission are fluorescence, phosphorescence, and induced luminescence. The last-mentioned radiative deactivation process is the foundation of the laser emission process, and it occurs only under specific conditions. The other two emissions are commonly observed and differ only for the change in multiplicity that occurs during the transitions. In a fluorescence emission, the initial and final state have a singlet multiplicity, whereas, in phosphorescence, the multiplicity changes from triplet to singlet.

Emission via fluorescence or phosphorescence is generally observed from the lowest electronically excited state, and, as previously mentioned, this behavior is connected to the energy gap law. The generalization of this observation falls under the name of Kasha's rule, which states that emission with an appreciable intensity takes place from the lowest excited state independently from the state to which a molecule is excited.

The inherent radiative lifetime of an excited state corresponds to the lifetime that an excited state would show without any competing processes other than the analyzed radiative deactivation, and it is inversely proportional to the transition dipole moment. Therefore, not-allowed or partially not-allowed transitions will have a longer radiative lifetime than formally allowed transitions. Since the emission via phosphorescence requires a change in spin multiplicity, it formally violates one of the above-mentioned selection rules and occurs at a slower rate than fluorescence. The inherent radiative lifetime of emission via fluorescence is normally between $10^{-9}$ and $10^{-5}$ s, where the slower transitions are typically forbidden for symmetry reasons. On the other hand, phosphorescence is usually characterized by radiative lifetimes greater than $10^{-5}$ s.

Nonetheless, two kinds of fluorescent emissions whose lifetimes exceed the expected values are known. The two phenomena were initially named P- and E-delayed fluorescence since they were first observed in pyrene and eosin, respectively. The reason behind the extended fluorescent lifetime of both emissions is the involvement of triplet excited states in their mechanisms. However, the role of the triplet states in the mechanism is different between the two delayed fluorescence emissions. P-type delayed fluorescence is based on the interaction between two excited molecules, both found in a triplet excited state (Fig. 3). Their interaction leads to a Dexter energy transfer that yields one molecule in its ground state and one in its excited singlet state, the radiative relaxation of the excited molecule finally generating the fluorescence emission. The multistep nature of the mechanism leads to an emission with a fluorescence lifetime longer than the one customarily observed. Due to the interaction involved, the mechanism leading to this fluorescence emission is known as triplet-triplet annihilation. Triplet-triplet annihilation can be used to achieve photon up-conversion and therefore found promising application in solar energy applications.
The emission processes this thesis focuses on is E-delayed fluorescence or thermally activated delayed fluorescence (TADF). A detailed discussion of the mechanism at the base of this phenomenon is presented in chapter 1.3. At this stage, is provided a simplified description that highlights the difference between TADF and triplet-triplet annihilation. TADF proceeds via an intermolecular process that only involves one molecule in its triplet excited state. A requirement for the emission to be observed is that the energy between T₁ and S₁ (ΔE_ST) must be in the same order of magnitude of the thermal energy of the environment (approximately 25 eV) or less. As will be later demonstrated, this rule has some important exceptions, but it corresponds to a condition used to design most of the known TADF emitters, including the molecules that are subject of this thesis. The energetical vicinity of the two excited states facilitates the thermally promoted up-conversion of T₁ to S₁ via rISC. Due to the low energy difference, the external environment can act as the heat sink and provide the energy for the excitation of T₁ to the vibrationally excited state required for the isoenergetic transition to S₁. The molecule found in S₁ then radiatively emits to the ground state via fluorescence emission. As in P-delayed fluorescence, the multiple stages of the emission mechanism lead to a fluorescence emission with a lifetime in the microsecond range that is remarkably more extended than the one customarily observed for standard fluorescence emissions.

![Diagram of TADF and triplet-triplet annihilation](image)

**Fig. 3** Schematic representation of the two types of mechanisms leading to delayed fluorescence emissions, triplet-triplet annihilation, and thermally delayed fluorescence.

### 1.2. OLEDs and TADF

Organic light-emitting diodes are devices that achieve light generation via the application of a voltage to a thin film of an organic substrate. The first observation of electroluminescence in organic molecules dates back to 1965 when Helfrich and Schneider reported that single crystals of anthracene would emit
light if an electric potential were applied via two electrodes.\textsuperscript{7} Other examples followed later in 1969 and 1970.\textsuperscript{8, 9} Despite the fundamental importance of these works in highlighting such an important phenomenon, the initially constructed “devices” needed an operating voltage of up to 100 V to generate the luminescence and displayed a remarkably low efficiency. The first practical example which can be considered the parent of modern OLEDs was reported in the pioneering works of Tang and Van Slyke in 1987.\textsuperscript{10} In the device developed by the researchers in the corporate laboratory at Kodak, a layer of aluminum tris-8-hydroxyquinoline was responsible for the emission, and the OLED displayed an operating voltage of less than 10 V.\textsuperscript{10} Since this key example, the research involving these devices flourished. Another significant milestone in this field can be considered the work of Friend and co-workers from 1990. In their publication, the researchers presented the first OLED based on a polymeric emissive material.\textsuperscript{11}

This chapter provides a brief illustration of the working principle of OLEDs and the development of this technology, which is helpful to understand the importance of TADF emitters in improving OLEDs’ performances.

1.2.1. General working principle and relevant parameters

The general architecture of OLEDs is derived from the one employed in inorganic light-emitting diodes (commonly referred to as LEDs), which chronologically have been the first solid-state lighting devices to be developed. Analogously to LED, OLEDs are based on a multi-layer structure. However, the inorganic materials serving the different functions are substituted with organic compounds. This chapter will focus on the central, light-emitting region of the stack, which in LEDs is represented by a p-n junction, whereas in OLEDs by an organic fluorophore.

The stacked structure of an OLED and the general working principle of the device are schematically represented in Fig. 4. It must be mentioned that the number of layers may vary between different devices since single layers may fulfill more than one function, or extra layers may be added to fulfill specific needs.

![Fig. 4 Schematic representation of the different layers present in an OLED device and of the operating principle of the device.](image)

At the two extremes of the device are found the electrodes, and one of them, usually the anode, is constituted by a transparent material to allow the emitted light to escape the device. The first layers after the electrodes are the hole and electron injecting layers. These regions facilitate the injection of the respective carriers by employing materials with appropriate energy levels for the HOMO (hole injection
layer) and LUMO (electron injection layer). In the more internal region of the stack are found the hole and electron transport layers. Their function is to facilitate the transfer of the respective carriers towards the emission layer and inhibit the movement of the opposite carrier towards the electrode. These layers have a double task; they avoid the carriers’ recombination in a different part of the device which is not the emission layer and avoid shunt currents. Occasionally, this layer may be substituted by two distinct layers of two different materials that fulfill only one of the two functions. These layers are then referred to as carrier transport and carrier block layer. At the OLED’s core the emission layer is found. Upon application of an electrical potential, holes, and electrons flow towards this region from the respective electrodes and recombine in this region, generating excitons. The radiative decay of the excited molecules is then responsible for the light emission, which escapes the devices through the transparent anode.

In the classic design of an OLED-based screen or light, three subpixels, each with one of the three colors red, green, and blue, are grouped to obtain a pixel capable of generating the entire color spectrum (RGB-OLED). For every subpixel, a different chromophore, emitting at a specific wavelength, is employed. A different approach consists in employing white subpixels, above which, a color filter is positioned to obtain the three-colors pattern. A white subpixel can be added to the three-colored subpixels to compensate for the light loss induced by the color filters. This design strategy takes the name of white OLED and color filters (WOLED-CF) or also color by white. This approach presents the advantage of lower production costs compared to the devices produced using the classic design. Devices based on a WOLED+CF architecture can be further divided into subcategories based on the strategy used to generate the white subpixels. The three main strategies for the generation of WOLEDS are: using the mixture of different chromophores in one single emission layer; using multiple emission layers, one stacked on top of the other; using tandem OLEDs in which two devices with two different emission profiles are stacked one on top of the other. A comparison between these three categories and a detailed comparison between RGB-OLED and WOLED-CF goes far beyond the scope of this thesis. More details about this topic can be found in the reported references.

A parameter that can be used to evaluate the OLED’s efficiency is the external quantum efficiency ($\eta_{ext}$) whereas a good indication of its stability is provided by the operational lifetime (LT). $\eta_{ext}$ is defined as the product of the internal quantum efficiency ($\eta_{int}$) and the light outcoupling efficiency ($\eta_{out}$) (Equation 3). $\eta_{int}$ is determined, in turn, by three factors, the charge carrier balance ($\gamma$), the emissive exciton production efficiency ($\eta_r$) and the radiative quantum yield $q$. The charge carrier balance expresses the offset of holes or electrons reaching the emission layer. The amount of both charge carriers should be balanced to ensure an efficient regime. Excess of charge implies the loss of electrical energy and can lead to detrimental quenching processes. The radiative quantum yield is a characteristic parameter of the chromophore and is the product of the competition between the different deactivation pathways involving the emitter’s excited state(s). The value assigned to $\eta_r$ depends on which percentage of the generated excitons can be used to produce light. According to spin-statistics, roughly 25% of the excited molecules are found in a singlet excited state upon electron-hole recombination, whereas the majority, 75%, are in a triplet excited state. If both excited states of the chromophore can lead to the production of light, the theoretical value associated to $\eta_r$ corresponds to unity. This factor greatly influences the diode’s efficiency, and its maximization is one of the primary aims of the research involving OLEDs. As reported later in greater detail (see chapter 1.2.3), $\eta_r$ can be maximized by either using phosphorescent or TADF emitters, which highlights the importance of these two emissions in the field of OLEDs. Lastly, the factor $\eta_{out}$ is defined by the ratio between the light emitted from the surface of the
device and the total light emitted by the emission layer. The light generated by the emission layer propagates in every direction, and a significant part is trapped inside the device due to the guiding effect of the different organic layers. Additionally, some of the emitted photons can leak from the side of the stack. By using emitters of the last generations, $\eta_{int}$ can theoretically reach unity. Therefore $\eta_{out}$, which normally assumes values close to 20%, is what greatly limits the efficiency of the devices.

$$\eta_{ext} = \eta_{int} \times \eta_{out} = \gamma \times \eta_r \times q \times \eta_{out}$$

Equation 3 Expression describing the different components which are contributing to the external quantum efficiency of an OLED.

Another relevant parameter used in evaluating the OLEDs’ performances is the operational lifetime which is used to estimate the stability of the emitters under the functional conditions. This parameter is indicated as LT_x and defined as the time to reach x% of the initial luminance under constant current operation. A factor directly related to the OLED’s operational lifetime is the stability of the emitter incorporated in the emission layer. Logically, devices built with more stable emitters are able to guarantee a longer operational lifetime which translates into a longer lifetime for the devices in which the diodes are embedded. The stability of a chromophore in an OLED is dictated by the intrinsic chemical properties of the molecule and by the energy and lifetime associated with its emissive excited state. The energy associated with the excited state of blue-emitting chromophores is close to the energy of the covalent molecular bonds in the molecule, which increases the possibility of bond cleavage. On the other hand, a longer lifetime increases the probability for the excited state to undergo deactivation via bimolecular processes such as triplet-triplet annihilation or polaron-exciton interaction. These events generate high-energetic hot states, which could lead as well to molecular dissociation. It follows that the lifetime of a diode can be improved by modifying the energy of the excited state or its lifetime. However, the energy of the excited state is often a fixed parameter since it is directly related to the wavelengt of the chromophore emission. On the contrary, the excited state lifetime can be influenced using different methods, and its modification has been shown to be a suitable way to extend the stability of an emitter embedded in an OLED and of the diode itself.

1.2.2. A brief comparison between OLEDs and LEDs in display applications

As a solid-state light-emitting technology, OLEDs find applications in display applications and, to a minor extent, in illuminating devices. In both fields, OLEDs strongly compete with their inorganic counterpart LEDs. A brief comparison of the two different types of diodes, when applied in display applications, is helpful to understand the differences between the two technologies and which aspects of OLEDs should be subjected to meliorative changes in order for them to compete with LEDs.

The technological advancement of flat panel displays based on both OLEDs and LEDs is far from being at a resting state. The research progress in this field follows a high pace, and private companies carry out a significant portion of the research effort. For these two main reasons, it is challenging to deliver an actual detailed description for both technologies that does not rapidly appear obsolete in some of its aspects. However, it is possible to delineate the significant fundamental points that differentiate OLED and LED displays.
The main differences between the displays based on the two light-emitting diodes are a product of the radically different flat panel architectures. LED-based displays rely on the combination of LEDs-based light sources and a liquid crystals display (LCD). The light generated by LEDs at the rear end of the display is diffused to obtain a homogeneous distribution over the screen area. The light is then transmitted by a light guide and polarized by the rear polarizer. The light polarization is then altered by the LCD in a controlled way depending on the voltage applied. Finally, the front polarizing filter transmits the light to the viewer according to its polarization. To generate a color image, the RGB components of the light are extracted by filters positioned between the LCD and the front polarizer, which generates the array of colored subpixels.\textsuperscript{12, 15, 30}

On the other hand, in OLED displays the diodes act as punctual light sources, and the luminosity of each pixel can be independently regulated. In these displays, the LCD and LED-based light source functions are combined. In small OLEDs displays, the subpixel color is determined by the chromophore employed in the emissive layer of the diode (RGB-OLEDs).\textsuperscript{12, 15, 30} For large screens where production cost and control of production inhomogeneity become critical aspects, an OLED-CF approach is used instead.\textsuperscript{13}

The advantages that each display technology offers are strongly related to the critical difference between the two architectures. Since LEDs can generally reach higher luminance levels than OLEDs, LCD displays are characterized by a higher brightness. At the time of writing, this display technology also presents lower production costs and more durability. The first aspect is related to the fact that LED displays are produced with an established process that has been greatly optimized. Even though the architecture of OLEDs-base displays is less complex, the production of the diodes still strongly relies on vapor-deposition techniques that are highly inefficient in terms of material utilization. To solve this problem, research efforts are directed towards establishing other production methods that ensure a more efficient material deposition. An alternative is represented by the so-called wet processes e.g., spin coating or inkjet printing. The second aspect, the durability of OLED displays, is principally influenced by the blue emitters’ stability and, in a minor way, by the diffusion of moisture in the devices. The high energy associated with the excited state of the blue chromophores leads to fast decomposition of the fluorophores and, therefore, to a faster color degradation. As previously reported, a way to improve the blue emitters’ stability is to reduce the blue chromophores’ excited state lifetime.\textsuperscript{12, 16, 30}

Even though OLED displays are far from being the perfect display technology, they present some significant advantages compared to LED displays that motivate the research aimed to improve these devices. Two of the most significant advantages are related to the absence of a rear illumination panel and the possibility of independently regulating the luminosity of each pixel. In LED displays, the presence of a constantly lit back-light source negatively affects the display’s power consumption and leads to light leaks through the dark pixels, which ultimately lowers the darkness of the black tones. On the other hand, in OLED displays the tone of black pixels is not degraded by a light source, leading to a maximal contrast and a superior image quality. Additionally, black pixels in OLEDs do not consume energy which allows minimizing the energy consumption of devices by developing dedicated “dark-modes” for programs running on devices that use OLED screens as interfaces.\textsuperscript{31} To bridge this gap, the manufacturers of LED displays developed rear light sources composed of separate small LEDs that can be locally dimmed in the dark areas of the image, thereby achieving similar results in terms of contrast to OLED displays.\textsuperscript{12} Another advantage of OLED displays is that, due to their simple architecture and the compounds employed in their construction, they are very flexible, and by carefully choosing the materials employed, they can even be used to produce transparent devices. These peculiar advantages allow the design of products that would
not be possible with any other technology, i.e., foldable displays or transparent screens. Lastly, it is also worth mentioning that the light generated by OLED displays has been demonstrated to produce lower ophthalmic toxicity. This effect was attributed to the lower amount of highly energetic blue light emitted by OLEDs compared to LEDs.  

1.2.3. Devices generations and application of TADF

Since the first reported device in 1987, OLED technology has been subjected to numerous improvements. One of the most significant elements used to improve the diodes’ efficiency is the type of chromophore(s) used in the emission layer. This parameter is also used as a marking element to distinguish between the different device generations, highlighting its importance in the technology’s evolution process. The succession of the different OLEDs generations with the corresponding type of chromophore employed in the emitter layer is schematized in Fig. 5.

![Fig. 5 Schematic representation of the different generation of OLEDs and the respective kind of emission that characterize the device generation.](image)

1.2.3.1. 1st generation OLEDs

The emitter used in the pioneering device reported by Tang and Van Slyke was tris(8-hydroxyquinolinato)aluminium (Alq3). This fluorophore and all the other molecules employed in the OLEDs of the first generation emit uniquely via fluorescence which implied that only excitons in a singlet excited state would lead to the production of light. Therefore, $\eta_r$ amounted to only 25%. This factor
strongly limited the external efficiency of the diodes that, in the case of the OLED of Tang and Van Slyke, amounted to 1.4%.

Fig. 6 schematic representation of the emission mechanism in OLEDs of the 1st generation.

1.2.3.2. 2nd generation OLEDs

As a logical step, a significant portion of the efforts spent on improving the OLED technology was directed to find emitters that could exploit both singlet and triplet excitons to produce light. Thompson, Forrest, and co-workers were the first to show that by using a transition metal-based phosphorescent emitter, also the energy of triplet excitons could be utilized without sacrificing the luminescent quantum yield.\(^{33}\) Previous devices based on keto-cumarines and benzophenone derivatives could also make use of triplet excitons but displayed extremely low \(\eta_{\text{ext}}\) (with values lower than 1%) due to the strong competition between radiative and non-radiative relaxation process.\(^{34,35}\) In the device presented in their work, Thompson, Forrest and co-workers used Alq\(_3\) as the host, DCM2 as the fluorescence luminophore, and a platinum(II)-porphine-based complex (PtOEP) as the triplet emitter which showed a phosphorescence efficiency of 0.5 when embedded alone in a polystyrene matrix.\(^{36}\) The authors could demonstrate that in their device, the non-emissive triplet excited state of Alq\(_3\), used as the host, could be almost completely transferred to PtOEP, which then emitted via phosphorescence. The implementation of this device architecture led to an OLED with \(\eta_{\text{ext}}\) and \(\eta_{\text{int}}\) of 4% and 23%, respectively.

Radiative relaxation of triplet excited states can be observed in transition metal complexes thanks to the presence of the heavy transition metal center that increases the spin-orbit coupling process, thereby allowing the transition from the excited triplet state to the ground state via phosphorescence. The presence of the transition metal center also increases the efficiency of the intersystem crossing from the singlet to the triplet excited state, reducing the amount of photons emitted via fluorescence.
The device presented by Thompson, Forrest and co-workers can be considered the first example of second-generation OLED. In another paper, the same authors showed how a nearly 100% internal quantum efficiency could be reached by using an iridium-based complex ((ppy)$_2$Ir(acac)), which further demonstrated the validity of this approach. Following this first example, many emitters based on transition metal complexes were developed, and platinum and iridium complexes proved to be the most efficient phosphors in this context.

The use of phosphorescence chromophores based on transition metal complexes in OLEDs solved the problem of converting the unutilized triplet state excitons into light emission. However, it proved to be difficult to produce blue emitters with satisfactory stability that would not lead to a high-efficiency roll-off of the diode in which they were utilized. This effect is partly caused by the significant energy associated with the excited state of blue-emitting chromophores and the relatively long lifetime of triplet excited states. One of the latest developed devices with a blue emitter showed a $T_{50}$ of 2203, which is still far from the ideal stability for practical display or lighting applications. Additionally, the use of not renewable and expensive transition metals is not optimal for a technology that aims to be used in display technology and eventually replace the omnipresent LED-LCD screens. For this reason, the research on alternative OLED emitters continued and aimed to find a class of chromophores that could guarantee the same efficiency of phosphorescence emitters without the need for transition metals and with higher stability.

1.2.3.3. 3\textsuperscript{rd} generation OLEDs and the central role of TADF

Even though some exceptions are known, it is relatively unusual for organic molecules to display room temperature phosphorescence. Additionally, phosphorescent organic materials generally display a relatively low luminescence quantum yield, making them unsuited substitutes to replace phosphorescent chromophores in OLEDs. It follows that, when using purely organic molecules, a different process other than room-temperature phosphorescence must be exploited to convert tripled excited states into light emission. The works published by Adachi and co-workers between 2009 and 2012 demonstrated how TADF constitutes a viable option.

TADF fluorophores can theoretically ensure full utilization of the generated excitons via a mechanism that, under some aspects, is opposite to the one used by phosphorescence emitters. In TADF emitters,
the generated singlet excitons can radiatively decay via fluorescence to the ground states as in the emitters used in the first-generation diodes. At the same time, the molecules found in the triplet state can also participate in the light emission since they can be up-converted to the singlet excited state via rISC, which is facilitated by a small \( \Delta E_{ST} \). The up-converted excited states can then participate in the generation of light via fluorescence emission. The validity of this concept was demonstrated in the work published by Adachi and co-workers where TADF emitter 1 (Fig. 11) and its analogs were used as emitters in OLEDs. The diode that employed 1 displayed a remarkably high \( \eta_{ext} \) of 19.3% and \( \eta_{int} \) was estimated to be between 64.3 and 96.5%, depending on the light outcoupling efficiency that was considered.\(^{42}\) This result could only be achieved if both singlet and triplet excitons took part in the diode’s fluorescence emission and evidenced the potential of TADF emitters in OLED technology. Additionally, the participation of triplet excited states in the emissive process via delayed fluorescence was supported by the photophysical characterization of the emitter and by the temperature dependence of their photophysical properties.

![Diagram](image.png)

*Fig. 8 Schematic representation of the emission mechanism in OLEDs of 3rd generation.*

Adachi and co-workers’ pioneering works paved the way for the development of the third generation of OLED devices based on TADF emitters and brought this kind of chromophores under the spotlight long after the first report regarding these emitters. The number of publications describing new TADF chromophores increased rapidly over the years, and both single molecules and polymers showing delayed fluorescence were implemented in OLEDs. A more detailed description of the TADF process in relation to the molecular structure of the emitters is reported later in chapter 1.3.

1.2.3.4. *The hyperfluorescence™ approach,*

Even though using TADF emitters leads to high internal quantum efficiency without employing transition metal complexes, the synthesis of a pure-blue OLED remained challenging due to the broad emission that characterizes these fluorophores. For reasons presented in greater detail in chapter 1.3, TADF chromophores often display emission peaks with ample full width at half maximum (FWHM), which negatively affects the color purity of the emitted light. A lower color purity of the emission requires additional technical solutions when the emitters are employed in displays (color filters or microcavities) to satisfy the color gamut standards.\(^{16, 37}\) This additional implementation may increase the device's fabrication cost or decrease emission efficiency. Therefore, emitters with a narrow emission are desired.
This aspect can be controlled by modifying the molecular scaffold of the emitter. As illustrated in chapter 1.3.1.4 in greater detail, the sub-class of TADF emitters, known as multi resonance emitters, can provide relatively narrow emission profiles thanks to their particular molecular structure.

However, modifying the molecular structure of TADF emitters is not the only way to improve the emitter’s color purity. An alternative approach known under the name of hyperfluorescence was presented by Adachi and co-workers in 2014.\textsuperscript{45} To avoid confusion, it must also be mentioned that prior to 2014, the same term had been occasionally used in the literature to indicate classical TADF emissions as well.\textsuperscript{46} The hyperfluorescence strategy that aims to improve the color purity of TADF-OLEDs consists in coupling a TADF chromophore with a standard fluorophore in the emitter layer. In this tandem system, the two components perform two different tasks that take advantage of the positive characteristics of each emitter (Fig. 9). The TADF chromophore allows energetic conversion and full exciton utilization, whereas the fluorescence dye is responsible for efficient fluorescence emission. Upon electron-hole recombination, the TADF emitter’s molecules are excited, and the triplet excited states are converted \textit{via} rISC to the singlet excited state. The energy of the singlet excited states is then converted \textit{via} Förster (or fluorescence) resonance energy transfer (FRET) to the singlet excited state of the fluorescence emitter. Lastly, the fluorescence emitter radiatively decays to the ground state generating the emission of light. The use of fluorescence emitters, which generally present a sharp emission peak, ensures a small emission peak’s FWHM and, therefore, high color purity. Additionally, the FRET reduces the time in which the TADF emitter’s molecules are in the excited state and the number of RISC/ISC cycles at the TADF emitter before radiative decay. For these reasons, adopting the hyperfluorescent tandem-system may also help decrease the excited state lifetime and, consequently, increase the stability of the TADF emitter.\textsuperscript{47}

![Diagram of emission mechanism in OLEDs of 4th generation](image)

This approach had also been expanded, generating more complex systems by using one or more exciples hosts in the emission layer, which involve multiple energy transfer steps. These changes aimed to increase the efficiency of the diodes by controlling the Dexter electron transfer (DET) processes which are detrimental for hyperfluorescent systems.\textsuperscript{48-50}

The validity of the hyperfluorescence approach was also recognized by the two most prominent companies that focus on developing efficient OLED emitters, the Japanese Kyolux and the German Cynora.
Both companies showed how the application of the tandem approach could indeed lead to the construction of more stable devices with a narrower emission.\textsuperscript{51, 52}

\section*{1.3. Organic TADF emitters}

The first documented observation of TADF could be found in a paper describing the delayed luminescence of eosin which dates back to 1930.\textsuperscript{53} However, this emission was properly characterized and interpreted as TADF only in 1961 in the work of Parker and Hatchard.\textsuperscript{3} After this first report, publications regarding this luminescence process in organic systems only appeared sporadically in the literature due to the lack of a relevant application.\textsuperscript{54, 55} The research on TADF emitters gained renewed attention only later, thanks to the pioneering works of Adachi and co-workers. Their series of works, published between 2009 and 2012, brought under the spotlight this peculiar emission by highlighting its great importance in the field of OLEDs technology (see also chapter 1.2).\textsuperscript{42-44} They demonstrated how employing TADF emitters in OLEDs could improve the efficiency of the devices without the need for transition metals which remarked the potential of these chromophores in such applications. The renewed interest in these emitters also stimulated investigations of the emission mechanism and contributed to the establishment of general rules for the molecular design of TADF emitters.

\subsection*{1.3.1. TADF and molecular structure}

\subsubsection*{1.3.1.1. The donor-acceptor architecture}

As already reported in chapter 1.1.4, TADF involves the thermally promoted up-conversion of a molecule found in its excited triplet state to one of its excited singlet states from which it then radiatively decays via fluorescence. Due to the endergonic nature of the process and the different spin multiplicities of the two states, the rISC process is favored by a small energy difference between the two states (\(\Delta E_{ST}\)) and by a big spin-orbit coupling. Without a heavy atom in their structure, classic organic emitters lack an element that could induce an efficient spin-orbit coupling between the singlet and triplet excited states. Consequently, minimization of \(\Delta E_{ST}\) via a rational design of the molecular scaffold plays an essential role in the development of such chromophores. In their early work dedicated to organic TADF emitters, Adachi and co-workers showed how a molecular structure based on a twisted donor-acceptor (DA) architecture could successfully yield emitters with a small value for \(\Delta E_{ST}\) and therefore lead to the emission \textit{via} TADF. Inspired by these first successful examples, most reported TADF emitters are designed according to this molecular design approach.

In DA structures, electron-donating and -accepting fragments are covalently linked, creating a molecular framework with separated electron-withdrawing and electron-accepting regions. In this kind of emitter, electronic excitation generates a charge-transfer excited state which, in first approximation, can be described as the transfer of one electron from the HOMO, localized on the donor, to the LUMO, localized on the acceptor. In the charge-transfer excited state, the two unpaired electrons are highly separated and, consequently, display a lower reciprocal influence. This last characteristic ultimately leads to a small energy difference between the singlet and triplet charge-transfer excited states indicated with \(^1\text{CT}\) and \(^3\text{CT}\), respectively.
More precisely, in DA molecules, the energetic separation between $^1\text{CT}$ and $^3\text{CT}$ ($\Delta E_{ST}$) can be considered proportional to the frontier orbital overlap and inversely proportional to the separation between the electron clouds of the two orbitals. Assuming that both the singlet and the triplet excited states share the same orbital wavefunction, the energy of the two excited states can be expressed as indicated in Equation 4a and Equation 4b. This assumption implies that $^1\text{CT}$ and $^3\text{CT}$ are characterized by equal orbital energy ($E_{\text{orb}}$) and Coulombic term ($K$). However, in accordance with Hund’s rules, the energy of $^1\text{CT}$ is higher than the one of $^3\text{CT}$, and this energy difference is expressed by the exchange term ($J$). As a result, $\Delta E_{ST}$ is solely proportional to $J$, as described by Equation 4c.

\[
a) \quad E_{^1\text{CT}} = E_{\text{orb}} + K + J \\
b) \quad E_{^3\text{CT}} = E_{\text{orb}} + K - J \\
c) \quad \Delta E_{ST} = E_{S_1} - E_{T_1} = 2J
\]

Equation 4 $E_{\text{orb}}$ is the orbital energy, associated to the one-electron orbital for a fixed nuclear geometry in the excited state, $K$ corresponds to the electron repulsion energy and is derived from the first order Coulombic correction, $J$ correspond to the exchange energy derived from the electron-electron repulsion according to the Pauli principle.56

In DA systems, the exchange term $J$ can be expressed in terms of the Dexter electron transfer theory, as reported in Equation 5. In the considered transition, $\Phi$ and $\psi$ correspond to the emitter’s HOMO and LUMO, respectively. The two numbers, 1 and 2, refer to the two indistinguishable electrons involved in the transitions, one remaining at the HOMO and the other being electronically excited to the LUMO. Lastly, $r$ refers to the spatial coordinates of the electron.56 As indicated by the reported equation, the value of $J$ depends on the distance between the two electrons and the overlap integral between $\Phi$ and $\psi$.

\[
J = \iint \psi(r_1)\psi(r_2) \left( \frac{e^2}{r_1 - r_2} \right) \Phi(r_1)\Phi(r_2) dr_1 dr_2
\]

Equation 5 Expression describing the exchange term for the transfer of an electron from orbital of a donor entity to the orbital of an acceptor entity. In the context of DA chromophores the two orbitals, $\Phi$ and $\psi$, can be approximated to the HOMO and the LUMO of the emitter, respectively.56

Combining Equation 4c and Equation 5 clearly shows that $\Delta E_{ST}$ proportionally depends on the spatial overlap between the HOMO and LUMO wavefunctions of the emitter, and it is inversely proportional to the distance between the electron clouds of the two orbitals.56-63 In DA molecules the HOMO and LUMO are highly localized on different parts of the structures, which ensures a certain degree of spatial separation and reduces their overlap. However, to efficiently minimize $\Delta E_{ST}$, the overlap between the frontier orbitals must be further reduced. As reported by Adachi and co-workers, this result can be achieved by twisting the two molecular units one respect to each other approaching an orthogonal arrangement. This arrangement reduces the conjugation between the acceptor and donor $\pi$ systems, which results in a misalignment between the two frontier orbitals and a reduction of their overlap. Eventually, the spatial separation between HOMO and LUMO can be enhanced by using a connecting fragment between the two moieties which further pushes the electron clouds of the two orbitals apart. Both the twisting of the donor and acceptor moieties and the use of a spacer are observed in the case of the TADF emitter 2 (Fig. 10).64 The presence of the methyl groups on the carbazole induces a torsion angle of 86.7° along the highlighted C-N bond and produces the reciprocal tilting between the two molecular regions. Additionally, the donor and acceptor fragments of 2 are separated by a phenylene linker.
Fig. 10 In compound 2 the overlap of the HOMO-LUMO orbitals is minimized thanks to the almost-perpendicular arrangement of the donor and acceptor fragments and by the spatial separation of the two moieties provided by the bridging phenylene fragment.54

1.3.1.1.1. Compound 1 in details

The donor-acceptor chromophore 1 (Fig. 11) is one of the first efficient TADF emitters developed by Adachi and co-workers and has been the object of numerous studies.42,65,66 The analysis of the emitter’s photophysical properties and their connection with the molecular structure exemplifies the previously presented concepts and illustrates the typical measurements employed in the characterization of TADF chromophores.

In the molecule structure of 1, the acceptor and donor fragments are represented by the central dicyanobenzene moiety and peripheral carbazole substituents, respectively. The steric repulsion between the two fragments induces the reciprocal rotation of the two molecular sub-units along the C-N axis and leads to a dihedral angle of about 60° between the carbazole units and dicyanobenzene planes. As confirmed by DFT calculations, the HOMO and LUMO orbitals are highly localized on the donor and acceptor fragments, respectively, and their overlap is minimized thanks to the reciprocal orientation of the two moieties (Fig. 11).42

Fig. 11 Molecular structure and frontier orbitals of 1. 42, 65, 66
In their work, the authors could prove that the adoption of this twisted-DA molecular architecture effectively led to the formation of a charge-transfer excited state and a small $\Delta E_{ST}$ which was estimated to be 83 meV (from the measurements in toluene solution).\textsuperscript{42}

The charge-transfer nature of the excited state was confirmed by the calculation of the natural transition orbitals (NTOs) for the chromophore and by investigating the influence of the solvent polarity on the emission wavelength. In the case of emissions taking place from charge-transfer excited states, the increase of the solvent polarity typically leads to a shift of the emission maxima towards lower energies, which is also referred to as positive solvatochromism. Thanks to the establishment of efficient polar interactions, solvents with higher polarity stabilize the highly polarized charge-transfer excited state, resulting in a bathochromic shift of the emission profile. Positive solvatochromism was indeed observed in the case of compound 1. Specifically, its emission maxima shifted from 507 nm to 544 nm to 565 nm by changing the solvent from toluene to DCM to acetonitrile.\textsuperscript{42, 67} Another characteristic that is typically displayed by emissions related to charge-transfer excited states is a large Stokes shift. However, this characteristic was not displayed by 1. The authors attributed this behavior to a reduced relaxation of the molecular structure upon excitation.

The emission via TADF for this chromophore could be confirmed by coupling the excited state lifetime measurements obtained via time-correlated single-photon counting (TCSPC) measurements with the results provided by steady-state emission spectroscopy. In the TCSPC measurements performed under inert conditions, two different decay regimes could be observed, which are referred to as prompt and delayed components (Fig. 12a). The prompt component (with a related lifetime of $17.8 \pm 1$ ns) is connected to the prompt fluorescence emission generated by the molecules which had been photoexcited directly to $^1$CT and that subsequently radiatively decay to the ground state. The delayed component (with an associated lifetime of $5.1 \pm 0.5$ $\mu$s) is also generated by the radiative decay of molecules in $^3$CT. These molecules, however, are initially found in $^3$CT and only later converted to $^1$CT via rISC. To unquestionably confirm the observation of TADF, however, the results collected via this first measurement must be supported by other experiments. Two main points must be verified: the emissions of the prompt and delayed components are taking place from the same excited state, and if triplet excited states are involved in the emission. Additionally, Monkman and co-workers also suggest excluding the involvement of triplet-triplet annihilation processes by analyzing the dependency of the emission intensity from the intensity of the exciting source.\textsuperscript{68}

The confirmation that for 1 both, the prompt and delayed emissions originate from the same excited state was delivered by the measurement of prompt and delayed fluorescence spectra, which perfectly superimposed (Fig. 12c). The involvement of triplet excited states was instead proven by the measurement of the excited state lifetime in the presence and absence of oxygen. Under aerated conditions, the triplet excited states and, consequently, the delayed emission are quenched due to the interaction with oxygen. Therefore, the presence of oxygen should ultimately lead to a reduction of the emission intensity and to a considerable reduction of the delayed component observed in the TCSPC measurements. In the case of 1, the lifetime associated with the delayed component measured in an aerated solution ($91 \pm 3$ ns), was considerably shorter than the one measured under inert conditions, which confirmed the strong quenching effect of oxygen on the delayed emission(Fig. 12a).

Due to the endergonic nature of the process, temperature has an important influence on the TADF emission. Investigating the dependence of the emission quantum yield and lifetime from the temperature
can further confirm the emission via TADF and be used to calculate two important parameters, namely, \( \Delta E_{ST} \) and the rate constant related to the reverse intersystem crossing process \( (k_{RISC}) \). For 1, the photoluminescence quantum yield of the prompt fluorescence only slightly increased as the temperature was lowered, possibly due to the suppression of non-radiative relaxation decays. Instead, the photoluminescence quantum yield associated with the delayed component decreases monotonously (Fig. 12b). This result further validates the thermally promoted character of the delayed emission. The authors also used the measurements of the photoluminescence quantum yield at different temperatures to calculate \( k_{RISC} \) and \( \Delta E_{ST} \), via the Arrhenius equation, which delivered \( 4 \times 10^7 \text{ s}^{-1} \) and 83 meV as results, respectively.\(^{42}\)

Fig. 12 Photophysical characterization of compound 1, the graphs are reported without any modification from the original publication.\(^{42}\) a) Influence of oxygen on the excited state lifetime. The presence of oxygen clearly quenches the delayed component of the emission confirming the involvement of triplet excited states in the radiative decay. b) Influence of the temperature on the global photoluminescence quantum yield and its delayed and prompt component. The effect of the temperature highlights the thermally promoted nature of the delayed fluorescence. c) Profile of the prompt and delayed emission spectra. The measurement confirms that both radiative decays originate from the same excited state.

A vast number of efficient TADF emitters based on a donor-acceptor structure were reported in the literature, confirming the efficacy of this molecular design. However, it must be noted that the adoption of the twisted-DA molecular architecture also presents two significant shortcomings: a broad emission profile and an intrinsic limitation of the fluorescence efficiency. The first point is connected to the charge transfer nature of the excited state. A charge-transfer excited state is subject to a high electron redistribution upon excitation, which may induce a high vibrational relaxation and, therefore, a broad emission profile. However, this issue does not affect all DA-TADF emitters, as proven by the several narrow-band DA chromophores reported.\(^{69}\) As discussed in chapter 1.2, a broad emission profile mainly affects the applications of TADF emitters in display devices.
What restrains the emission efficiency is instead the small overlap between the frontier orbitals. The overlap between HOMO and LUMO not only plays an essential role in influencing the value of $\Delta E_{ST}$, but it is also linked to the fluorescence rate constant ($k_f$). The magnitude of $k_f$ and the frontier orbitals overlap are connected through the transition dipole moment of the radiative transition. The transition dipole moment is, in fact, directly proportional to the spatial overlap between the orbitals of the excited and ground state (1.1.4), which in this case, could be approximated to the LUMO and HOMO, respectively. If, on one side, diminishing the overlap between the two wavefunctions leads to a beneficial reduction of $\Delta E_{ST}$ and consequently to an increase of $k_{rISC}$, it also induces a detrimental reduction of $k_f$ due to the reduction of the related transition dipole moment. A similar situation is, for instance, observed also aromatic ketones such as benzophenone where the orthogonal arrangement of the $n$ and $\pi^*$ orbitals greatly limits their overlap and leads to a small energy difference between the singlet and triplet excited states. However, their photoluminescence quantum yields are generally low as a result of the low overlap between the $n$ and $\pi^*$ orbitals. It is, therefore, evident how the overlap between the frontier orbitals affects the performances of TADF emitters in two opposite ways.

In TADF emitters, the two rate constants $k_f$ and $k_{rISC}$ are strongly interconnected, and a balance between the two related processes must be found to guarantee both an efficient rISC and an intense fluorescence emission. One way to ensure a high $k_f$ despite the small frontier orbital overlap is to inhibit the non-radiative deactivation pathways, which favors the radiative emission. Therefore, suppression of non-radiative relaxation pathways has a critical role in TADF emitters together with the minimization of $\Delta E_{ST}$. To limit the non-radiative relaxation of the excited state, its vibronic coupling with the ground state should be reduced. This result can be achieved by adopting a rigid structure or limiting the vibration of the flexible part of the scaffold. In the specific case of compound 1, the structure is not rigid since the carbazole substituents can rotate along the N-C bond. However, the steric interactions between the different carbazole substituents inhibit their rotation and ensure a high fluorescence intensity, leading to a photoluminescence quantum yield of 93.8%.

1.3.1.2. The connection between $rISC$, locally-excited states (LE), and molecular vibration

Since compound 1 was reported in 2012, the research on TADF emitters has seen rapid growth. Researchers did not only concentrate on the expansion of the emitter's palette but also on the detailed investigation of the mechanism responsible for the delayed emission. Developing a model that would accurately describe the factors influencing the TADF emission is essential for the rational improvement of the chromophores' performances. Initially, the simple two-state mechanism proposed by Parker and Hatchard in 1961 and then evolved by Adachi and co-workers seemed to adequately describe the TADF dynamics. In this model, only one singlet excited state, from which the emission takes place, and one triplet excited state are included. $k_{rISC}$ can then be described according to Fermi's golden rule (Equation 6). Equation 6 is derived from the first-order perturbation theory, assuming the coupling of the initial and final states to be small compared with their energy difference and considering the Condon approximation to be valid. $k_{rISC}$ depends on the magnitude of the spin-orbit matrix element ($R_{SOC}$), on the adiabatic energy difference between the two excited states and on the coordinate displacement of the singlet and triplet potential energy surfaces ($v_{rISC}$ and $v_{S}$ respectively). The dependency of $k_{rISC}$ from the energy difference between the two states ($\Delta E_{ST}$) is more evident if the mixing coefficient ($\lambda$) is considered. In the context of the perturbation theory, $\lambda$ indicates the probability for the transition between the two states to occur; therefore, a higher value for this parameter corresponds to a higher rate of the transition. $\lambda$ itself is
directly proportional to the strength of the perturbation and inversely proportional to the energy difference between the considered states, taking into account its relation with the rISC rate yields: 

\[ k_{rISC} \approx \left| \frac{\langle \psi_T | \hat{H}_{SOC} | \psi_S \rangle}{\Delta E_{ST}} \right|^2. \]

\[ k_{rISC} = \frac{2\pi}{3h^2} \sum_f \left| \langle \psi_T | \hat{H}_{SOC} | \psi_S \rangle \right|^2 \sum_{k,j} e^{-\beta E_k} \left| \langle \nu_{Tk} | \nu_{Sj} \rangle \right|^2 \delta (E_S - E_T) \]

Equation 6 Reverse intersystem crossing rate constant \( k_{rISC} \) expressed in terms of Fermi’s golden rule. \( Z = \sum e^{-\beta E_i} \) is a canonical partition function for vibrational motion in the initial electronic state, \( \beta \) is the inverse temperature, and \( E_i \) is the energy of the vibrational level in the initial electronic state. The factor of 3 in the denominator of Eq. (8.4) takes care of the degeneracy of the triplet sublevels.\(^{72}\)

As mentioned before, organic molecules without a heavy atom in their structure do not display a significant spin-orbit coupling. Consequently, when designing new TADF emitters, the reduction of \( \Delta E_{ST} \) had a central role. However, as the research on this class of emitters progressed, discrepancies between the calculated values for \( k_{rISC} \) and the one obtained experimentally were observed.\(^{76}\) Additional inconsistencies were also observed in the calculation of \( \Delta E_{ST} \) with two different methods, namely by using the Arrhenius equation and by measuring the energy difference between the onset of the fluorescence and phosphorescence spectra of the emitter.\(^{77}\) The work of Bryce and co-workers further highlighted the weakness of the initially proposed model. In their work, the researchers synthesized different emitters with similar \( \Delta E_{ST} \) values but different molecular rigidity.\(^{78}\) Even though the emitters displayed similar \( \Delta E_{ST} \), their photophysical properties were remarkably different. Some chromophores even showed only a weak TADF emission and primarily luminesced via room-temperature phosphorescence (RTP), which clearly indicated how \( \Delta E_{ST} \) is not the only parameter determining the efficiency of the delayed emission.

One of the critical points of the interpretation involving the simple up-conversion from \( T_1 \) to \( S_1 \) is that the spin-orbit coupling between the two states is extremely inefficient and cannot justify the intersystem crossing rates reported in the literature. The change in spin multiplicity should be, in fact, counterbalanced by a change in the orbital angular momentum to satisfy the principle of conservation of total angular momentum. Being both \( S_1 \) and \( T_1 \) charge-transfer excited states the change in spin angular momentum cannot be offset by a change in orbital angular momentum, therefore, leading to a vanishing spin-orbit coupling matrix (which translates to \( \langle \psi_T | \hat{H}_{SOC} | \psi_S \rangle = 0 \) in Equation 6).\(^{68, 79, 80}\) The same conclusion can be drawn by considering the transition in the frame of El-Sayed rules for which the (reverse) intersystem crossing between two states with the same character is formally forbidden. An alternative possibility that had been proposed is for the up-conversion to proceed via hyperfine coupling.\(^{81}\) While this would potentially allow a higher rate for the intersystem crossing, this phenomenon is only possible when the energy difference between the two excited states is extremely low. It cannot be excluded that, for some emitters, this kind of coupling could play a major role in their delayed emission. However, many emitters reported in the literature did not display the low value for \( \Delta E_{ST} \) required for hyperfine coupling to take place.\(^{80}\)

To provide a better model for the TADF emission, researchers turned their attention to the factors that, other than \( \Delta E_{ST} \), seemed to influence the delayed emission. For instance, the outcome of the above-mentioned work of Bryce and co-workers suggested that the rigidity of the molecular scaffold and, therefore, molecular vibrations may have a significant role in the TADF mechanism. This would imply that the Frank-Condon approximation, on which Equation 6 is based, may not apply to these systems. Another relevant observation that must also be mentioned is the one reported by Monkman and co-workers.\(^{77, 82}\)
In their work, they showed that by changing the polarity of the environment in which the emitter was embedded, the energy of the excited states involved in the TADF mechanism could be independently modified. This behavior would suggest that the states involved in the TADF emission did not possess both a charge-transfer character or that additional excited states were involved in the rISC process. Based on these elements, two different new models had been proposed in alternative to the initial description.

1.3.1.2.1. The vibronic-coupling model

In their model, Gibson et al. did not only include the singlet and triplet charge-transfer excited states $^3$CT and $^1$CT, but also a locally-excited state with a $^3\pi^*$ character ($^3$LE). In their work, the authors used these three excited states to set up a model Hamiltonian which could be successfully used to model the rISC rate of one previously reported TADF emitter and establish a more detailed description regarding the mechanism of the delayed emission for this chromophore.

In their quantum dynamic study, the authors could highlight that the vibronic coupling between $^3$CT and $^3$LE is essential for rISC to take place and that a model based on first-order perturbation theory (Equation 6) was not enough to describe the rISC process. To accurately model the rISC process, a second-order term proved to be essential (Equation 7). The authors additionally demonstrated that hyperfine coupling only minimally contributed to the delayed emission of the chromophore.

$$a) \quad k_{\text{rISC}} = \frac{2\pi}{\hbar} \left| \langle \right|^3\psi_{\text{LE}} \hat{H}_{\text{vib}} \left| ^3\psi_{\text{CT}} \rangle \right|^2 \times \delta \left( 3E_{\text{LE}} - 3E_{\text{CT}} \right)$$

$$b) \quad k_{\text{rISC}} = \frac{2\pi}{\hbar} \left| \frac{1}{\delta \left( 3E_{\text{LE}} - 3E_{\text{CT}} \right)} \langle \right|^3\psi_{\text{CT}} \hat{H}_{\text{SOC}} \left| ^3\psi_{\text{LE}} \hat{H}_{\text{vib}} \left| ^3\psi_{\text{CT}} \rangle \right|^2 \times \delta \left( 3E_{\text{CT}} - 3E_{\text{CT}} \right)$$

Equation 7 First order (a) and second order (b) components used to describe the reverse intersystem crossing rate constant $k_{\text{rISC}}$.

According to the model reported by Gibson and co-workers, the rISC process formally proceeds over two stages. Firstly, the first-order coupling between $^3$CT and $^3$LE, which is much larger than the one between the two charge-transfer excited states, leads to a rapid equilibrium between the populations of the two triplet states (Equation 7a). Only after the establishment of this equilibrium, $^1$CT and $^3$CT are coupled by the second-order perturbation term (Equation 7b). This second-order term is very efficient in comparison to the spin-orbit coupling part of Equation 6 because of the excellent vibration overlap between the almost degenerate $^3$CT and $^3$CT. In this model, the locally-excited state fulfills a vital mediator role and can be either centered on the donor or the acceptor.

From the analysis of Equation 7, two major considerations about this model, and therefore the TADF process, can be extrapolated. Firstly, the rISC process’s efficiency is determined not only by $\Delta E_{\text{CT}}$ but also by the energy difference between $^3$CT and $^3$LE ($\Delta E_{\text{CT}-\text{LE}}$). According to the model, the contribution of locally-excited states is essential for rISC to take place, and its energy should also be considered when designing these chromophores. If an efficient vibronic coupling between $^3$CT and $^3$LE is provided, rISC will take place independently from the relative position of the two excited states on the energy scale. Additionally, the coupling between the two states, and therefore $k_{\text{rISC}}$ will increase if the energy difference between the states is diminished. As observed in different cases, increasing the difference in energy between $^1$LE and $^3$CT reduces $k_{\text{rISC}}$, which is reflected in a longer lifetime for the delayed fluorescence emission ($\tau_{\text{TADF}}$). A long $\tau_{\text{TADF}}$ is detrimental since it increases the chances of the emitter to be quenched via bimolecular processes or undergo non-radiative deactivation, which limits its photoluminescence quantum yield (PLQY). Additionally, as reported in chapter 1.2.1, a long excited state lifetime also has a direct
negative influence on the stability of the emitter when embedded in an OLED, which leads to a short operating time of the diode.

Another critical point of this model concerns the critical role of molecular vibration in the TADF mechanism. The model developed by Gibson et al. shows that molecular vibration is essential to promote the population of the mediator state \(^3\)LE, making them indispensable for the delayed emission to take place.\(^{29}\) From this analysis, it also emerges that the rISC mechanism cannot be described with simple ladder transitions between different states as in the classical depiction of a Jablonski diagram. Instead, the combination of spin vibronic and nuclear dynamics leads to the mixing of different levels through which the rISC takes place. The model additionally explains how emitters with relatively large values of \(\Delta E_{ST}\) can still display efficient TADF. It is, in fact, possible to obtain a high value for \(k_{\text{rISC}}\) at the conditions that an efficient vibronic coupling with the locally-excited state can be established and that \(\Delta E_{\text{CT-LE}}\) is minimized.

The validity of this model could be supported by experimental measurements performed via photoinduced absorption, and it also found confirmation on EPR measurements performed prior to the establishment of the model itself.\(^{81, 86}\) This description provides a better understanding of the TADF process and clarifies how factors as the molecular rigidity or the polarity of the environment could influence the delayed emission. By restraining the molecular motion, the vibronic coupling with the locally-excited state is hindered, which leads to an inhibition of TADF in favor of other processes. This led, for instance, to emission \(\text{via}\) RTP for some of the emitters developed by Bryce and co-workers.\(^{28}\) The above-mentioned observation reported by Monkman and co-workers could also be explained by this model.\(^{82, 87}\) Due to their different nature, charge-transfer and locally-excited states are differently influenced by the polarity of the environment. Therefore, the energy difference between the local and the charge-transfer excited states, and consequently \(k_{\text{rISC}}\), can be altered by changing the polarity of the medium in which the emitter is contained. The model developed by Gibson et al. could also explain the difference between the values of \(\Delta E_{ST}\) calculated with the two approaches. Even though Adachi et al. proposed that this difference is caused by the molecular reorganization of the relatively long-lived triplet excited state, it could also be caused by the involvement of the locally-excited state in the delayed fluorescence emission. An efficient coupling would lower the activation barrier for the process, which would not be determined by \(\Delta E_{ST}\) but by \(\Delta E_{\text{CT-LE}}\).

This new interpretation of the TADF process expanded the knowledge of the dynamics behind the delayed emission and had a strong influence on the design approach towards new TADF emitters. While the design of the first architectures was focused on the minimization of the HOMO-LUMO gap to obtain a small value of \(\Delta E_{ST}\), in the design of new emitters, the energy of the locally-excited states as well as the molecular flexibility are also considered as relevant factors. The possibility for an emitter to achieve efficient rISC with relatively large values of \(\Delta E_{ST}\) enabled a more flexible design approach that optimized the efficiency of rISC without excessively compromising the efficiency of the fluorescence emission. An elegant example of the integration of this model in the design process of TADF emitters is presented in the work of Narsaria et al.\(^ {88}\) In this work, systematic modifications of the molecular structure of boron-based emitters were implemented in order to modify the energy of the locally-excited state together with the molecular geometry. The donor-spacer-acceptor structure of the chromophores allowed to selectively modify the energy of the locally-excited state centered on the spacer without inducing significant changes in the energy of the charge transfer excited state and, therefore, the emission wavelength of the emitter. Additionally, the authors could also develop an in-silico protocol that was used to determine the energy
difference between the different excited states involved in the emission process, thereby forecasting the
effects of the molecular changes on the emission properties.

1.3.1.2.2. The four-states model

An alternative interpretation of the mechanism for the rISC process in a TADF emitter is delivered by the
model developed by De Silva et al. The authors developed a four-states model which includes in its
description four different excited stated in contrast to the initial two-state model involving only 1CT and
3CT. The Hamiltonian developed by De Silva et al. incorporates four different-spin mixed diabatic states
that represent both pure charge transfer and local excitation (CT1, CT2, LE1, and LE2). Analogously to the
model of Gibson, the four-state model acknowledges the importance of including locally-excited states in
the description of the rISC process; however, this model does not require the non-adiabatic mixing
between the considered states to explain the TADF emission. The authors promptly specified that their
description is not meant to be universal and that it is not excluded that non-adiabatic coupling may play
an essential role in some systems. The expression for \( \Delta E_{ST} \) obtained from the Hamiltonian of the four-
states-model (Equation 8) includes all the parameters of the model itself and is not simply dependent on
the exchange integral as in the two-states model. As the previously illustrated model, this description
shows that minimizing the HOMO-LUMO overlap is not the only way to reduce \( \Delta E_{ST} \) and that additional
parameters should be considered.

\[
\Delta E_{ST} = K_{LE} + K_{CT} - \frac{1}{4} (\Delta E + K_{LE} + K_{CT})^2 - (\Delta E + K_{LE} + (t + K_x)^2
+ \frac{1}{4} (\Delta E - K_{LE} - K_{CT})^2 - (\Delta E + K_{LE} + (t - K_x)^2

\text{Equation 8} \Delta E \text{ is the energy gap between CT and LE states where the energy of CT is arbitrary set to zero. The other exchange}
\text{integrals are defined as: } K_{CT} = \langle CT1 | \hat{H} | CT2 \rangle, K_{LE} = \langle LE1 | \hat{H} | LE2 \rangle, K_x = \langle CT1 | \hat{H} | LE1 \rangle \text{ and } t = \langle CT1 | \hat{H} | LE2 \rangle \text{ they are a sum}
of a one-electron hopping integral and a two-electron integral.}

A key element of the description of De Silva and co-workers is that CT and LE states of different
multiplicity have different mixing strengths. Therefore, excited states of the same type can have a
different electronic character depending on their multiplicity. The most important implication of this
difference is that, in these cases, the SOC matrix between 1CT and 3CT is not negligible anymore as in the
case of pure charge-transfer excited states. Therefore, according to this model, SOC can be in principle
appreciable also without the mediation of an additional triplet excited state. This aspect of the model is
in line with the reports of TADF emitters, where the lowest triplet state is found to have a strong LE
component which is not found in the singlet state. Another aspect that validates the four-states model
is the prediction of negative values for \( \Delta E_{ST} \). Such peculiar characteristics could indeed be observed in
molecules similar to the model system considered by De Silva as reported by Sanz-Rodrigo et al.

As the developers of the two different models mentioned, the two descriptions do not exclude each
other; instead, different systems may be better described by one model or the other. The key message is
that the rISC process and, consequently, TADF are governed by much more complex dynamics and
parameters than initially considered. Both models show that multiple variables influence the rate of the
rISC process and the performances of TADF emitters. Therefore, when designing the structure of a new
TADF chromophore, the attention should not be solely concentrated on reducing the value of \( \Delta E_{ST} \) but
also on the energy, electronic character, and interaction of other orbitals and on molecular flexibility.
The donor-acceptor architecture and the emission wavelength

The great research effort directed towards TADF emitters in the last decade resulted in the synthesis and characterization of a great variety of chromophores. Even though alternative molecular architectures had been developed (see chapter 1.3.1.4), the donor-acceptor arrangement was and still is extensively applied in the creation of new TADF emitters. A wide number of molecular fragments and functional groups had been screened for both the donor and acceptor units, and a wide range of combinations had been tested. In Fig. 13, is presented a small summary of the most frequently used donor and acceptor fragments, a more exhaustive list is present in the indicated references.\textsuperscript{93-97} Due to the intrinsic electron-deficient nature of boron, fragments based on this heteroatom had found an extensive application in TADF emitters. At the end of this chapter, a small section is dedicated to the moieties containing this heteroatom (chapter 1.3.1.3.1).

Each moiety possesses peculiar electronic and structural characteristics that directly impact the photophysical properties of the DA emitter in which they are combined. In this section, the focus is set on the connection between the employed fragments and the emitter’s emission wavelength.

As previously mentioned, in donor-acceptor structures, the HOMO and LUMO orbitals are highly localized on the donor and acceptor fragment, respectively. Due to the strong spatial segregation and localization of the frontier orbitals, their energy and the energy of the corresponding fragments are strongly connected. Specifically, the HOMO of the emitter has a similar energy to the HOMO of the donor; the same consideration is valid for the LUMO of the emitters and the acceptor’s LUMO (Fig. 14).\textsuperscript{98} It follows that a change in the electronic properties of one of the two fragments mainly influences one of the frontier orbitals’ energies. Therefore, within certain limits, the choice of the donor and acceptor fragments can be used as a tool to modify the energies of the HOMO and LUMO selectively.

As previously mentioned, in DA emitters, the formation of the charge-transfer excited state can be approximated to the excitation of one electron from the HOMO to the LUMO and the fluorescence
emission to the opposite process. A change in the electronic properties of the donor or acceptor fragments influences the frontier orbitals’ energies and consequently the energy associated with the fluorescence emission.\cite{97, 99, 100} For instance, employing a stronger acceptor fragment (with a less energetic LUMO) would induce a reduction of the energy associated with the emitter’s LUMO, thereby causing a red-shift of the emission. On the contrary, employing a weaker acceptor fragment will cause an increase of the LOMO energy and consequently a blue shift of the emission (Fig. 14). A similar situation is observed for the donor fragment which electronic properties influence the energy of the emitter’s HOMO. Also in this case, an increase of the fragment’s donor strength corresponds to a red-shift of the emission, whereas a decrease of the fragment’s donor strength to a blue-shift of the emission.

![Fig. 14 Schematic representation of the energy levels of a DA emitter in relation to the energy level of the individual fragments. The scheme also exemplifies the influence of the acceptor strength on the energy of the emission. The use of a stronger acceptor leads to a decrease of the HOMO-LUMO energy of the emitter and, therefore, to a red-shift of the emission. The use of a weaker acceptor leads to the opposite effect and, therefore, to a blue-shift of the emission.](image)

The possibility of tuning a chromophore emission’s wavelength is advantageous since it makes it possible to match the emission’s color with the one required by its application. As illustrated above, in DA chromophores, the wavelength of the emitted light can be tuned by modifying the strength of the acceptor or donor fragments. The design of a flexible synthesis path that allows the straightforward modification of one of the two molecular fragments would allow to tune the emission wavelength according to the desired value without establishing a new synthesis route or developing a new emitter. Two general synthesis strategies can be adopted to reach this goal (Fig. 15).

The first strategy implies the development of a straightforward synthesis path in which the donor or acceptor fragments can be conveniently exchanged by employing different starting materials.\cite{101-104} For instance, this strategy was employed by Yasuda and co-workers. The authors established a synthesis sequence thanks to which they could synthesize a series of 5 different compounds characterized by different combinations of donor and acceptor fragments by simply exchanging the partner of the main coupling reactions (e.g. see compounds 3, 4, 5, and 6, Fig. 15). The obtained emitters presented HOMO-LUMO energy differences between 2 and 3.2 eV and, accordingly, displayed emission at different wavelengths. The fluorescence maxima of the chromophores embedded in polymeric thin films were distributed homogeneously between 450 and 610 nm, covering a wide range of the visible spectrum.
The second approach implies the synthesis of an emitter that acts as a precursor and is subsequently transformed into different emitters via a suitable derivatization reaction.\textsuperscript{105, 106} This approach was, for instance, applied by Bräse and co-workers.\textsuperscript{106} The well-known TADF emitter 1 was modified with sodium azide to yield compound 7 (or eventually also the mono derivatized analog), which was used as the precursor in the reaction with different acyl chlorides. The net result of the two reactions corresponds to the substitution of the nitrile substituents in 1 with different oxadiazoles (compound 8 Fig. 15) fragments. As in the previous example, this synthesis approach was used to synthesize a wide variety of emitters with different HOMO-LUMO energies and, consequently, emission wavelengths. This last strategy may be particularly appealing if the synthesis towards the molecular structure is demanding or if the desired fragments contain functional groups that are not compatible with the main synthesis path. Both approaches can be found in the literature. However, the first strategy is more frequently employed. Due to their aimed application in OLEDs, the synthesis pathways used for the production of TADF emitters are designed to be cost-effective and straightforward. For this reason, the synthesis sequences are generally simple and constituted of a few steps, which reduces the advantages offered by the second strategy.
Fig. 15 Exemplification of the two strategies that can be used to synthesize chromophore libraries in which the emitters are characterized by different emission wavelengths. The emission profiles of the compounds highlight the broad area of the visible spectra covered by the emission of the various derivatives. The graphs are reported without changes from the cited references.104, 106

1.3.1.3.1. Boron-based acceptor moieties

When discussing this emitters’ class, it is worth mentioning the relevance of boron in this context and, more specifically, concerning the construction of the acceptor moieties. Even before the rise of interest in organic TADF emitters, both tri- and four-coordinated organoboron compounds played a significant role in the field of optoelectronic and emissive materials.107-109 Possibly, the most known
representatives of this class are boron dipyrromethene dyes (BODIPYs) which are widely employed thanks to their high fluorescence quantum yield and narrow emission.\textsuperscript{110,111}

In the context of DA emitters, moieties containing both tricoordinated and four coordinated boron atoms have been successfully employed as acceptor fragments (Fig. 13 and Fig. 16). In tricoordinated boron compounds, the presence of an empty $p$ orbital at the boron atom renders the boron center an efficient $n$ acceptor, which ultimately determines the electron-accepting character of the fragment. At the same time, the empty $p$ orbital renders the boron atom vulnerable towards nucleophilic attacks, and adequate steric protection around the heteroatom must be provided to ensure the stability of the emitters.

Moieties based on tetracoordinated boron had also been successfully employed in push-pull systems even though, in these fragments, the empty $p$ orbital of the boron center is saturated by the lone pair of a heteroatom (i.e. oxygen or nitrogen). In these compounds, the heteroatom is integrated into a conjugated backbone which acts as a bidentate substituent. The formation of the chelated compound protects the boron center from nucleophilic attacks and stabilizes the $\pi^*$ orbital of the conjugated system, which ultimately infers the electron-accepting character to the fragment. Additionally, the formation of the chelated adduct increases the rigidity of the moiety, which could lead to a suppression of non-radiative relaxation pathways and, therefore, an increase of the radiative efficiency of the emitter.

The numerous works dedicated to tricoordinated and tetracoordinated boron-based fluorescence emitters showed that such molecules’ electron-accepting character and emission wavelength could be easily tuned by modifying the substituents at the boron center.\textsuperscript{112} Such modifications can be implemented in DA-TADF emitters equipped with a boron-based acceptor fragment to modify the HOMO-LUMO energy difference, and consequently, the emission wavelength of the chromophores. With the help of some relevant examples, a small summary containing the most employed type of boron-based acceptor fragments is reported in Fig. 16. These moieties and consequently the emitters in which they are employed can be divided into two main macro-categories that differ in the coordination of the boron atom.

To the class of tricoordinated boron emitters belong compound based on triaryl- and diarylboranes (9 and 10) and 9,10-dihydro-9,10-diboraanthracene (15) moieties.\textsuperscript{113-115} Besides being the first reported example of a TADF emitter bearing a diboraanthracene-containing moiety, 15 represents a noteworthy example since the neat thin film of the emitter showed a remarkable photoluminescence quantum yield of 90.6%. Consequently, 15 could be used to construct a device that included only a monolayer of the neat emitter between the two external electrodes and still displayed high external quantum efficiency of 19%.\textsuperscript{116}

Other emitters belonging to this class have a boron-based donor moiety that contains the tricoordinated boron center and another heteroatom. Examples of these fragments are, for instance, phenoxaborines (11 and 12), phenothiaborines (13), phenoazaborines and 5,9-dioxa-13b-boranaphtho[3,2,1-de]anthracenes (14).\textsuperscript{117-121} Compound 12 represents another example, other than 15, in which two boron centers are present in a single acceptor unit, in this case, in the form of a ladder-oxaborine fragment.\textsuperscript{117} When embedded in a polymeric thin film, compound 12 proved to be an extremely efficient TADF emitter displaying a quantum yield of 100%. The high efficiency of the emitter is induced by the small value of $\Delta E_{ST}$ and by the favorable energy of a local triplet excited state located on the
oxaborine fragment. This excited state is close in energy to the $^3$CT state and can therefore assume the role of mediator in the rISC process as previously described.

The pyridyl-pyrrolide boron fragment was incorporated in the first-reported boron-based TADF emitters with a tetracoordinated boron atom (16). Later works made successful use of other fragments based on phenylpyridine (17), 2-(2-pyridinyl)phenolate (18) and 2,2′-(pyridine-2,6-diyl)diphenolate moieties (19). In the work dedicated to compound 17, the authors clearly demonstrated how the introduction of the boron atom in the molecular structure is directly responsible for the high performances of the emitter by comparing them with the one of the non-borylated analogue. The compound lacking the boron center does not display any delayed emission which is enabled once the heteroatom is introduced in the molecular structure. The coordination between the nitrogen and boron atom increases the LUMO’s polarization, decreasing the overlap between the frontier orbitals and leading to a small value of $\Delta E_{ST}$, thus enabling the emission via TADF.

The group of four-coordinate difluoroborane complexes is an important subclass of TADF emitters with a tetracoordinated boron-based acceptor fragment. In these molecules, a BF$_2$ fragment is bound to a suitable chelating substituent which may also be, in some instances, one of the fragments previously illustrated. Compound 20 constitutes a remarkable example of this group in that it is one of the very few examples of highly efficient TADF chromophores with an emission in the near-infrared region.
1.3.1.4. Alternative molecular-design approaches

In alternative to the molecular design illustrated in the previous sections, donor-acceptor systems can be obtained in two additional ways. The two additional strategies rely on the formation of exciplex or through-space charge transfer. In the first case, two distinct molecules are employed, one with an electron-withdrawing character, the acceptor molecule, and one with an electron-donating character, the donor molecule. Excitation of one of the two molecules leads to the formation of an electronically excited bimolecular complex (excimer). Since the electron and the hole are situated on two different molecules,
the excimer displays a small exchange energy integral and a small value of $\Delta E_{ST}$. As previously illustrated, a small $\Delta E_{ST}$ facilitates the thermally promoted rISC of the excited triplet state, leading to a TADF emission.$^{127, 128}$ Using this approach, some efficient TADF exciplex-systems had been reported. However, the devices built using such DA systems typically display lower quantum efficiencies than those built using the classical DA molecules. Moreover, the fabrication of the devices requires more optimization since the formation of excimers is highly influenced by the emitter’s concentration in the matrix.

The approach based on through-space conjugation is conceptually positioned between the classical DA and the DA-excimer approach. This alternative strategy relies on the formation of a sort of intermolecular excimer via through-space conjugation. In these systems, the donor and acceptor fragments are in the same molecule but are not conjugated as in standard DA emitters. The establishment of the DA interaction occurs via through-space charge transfer and, as in DA-excimers, the great separation of the electron and the hole ensures a small value of $\Delta E_{ST}$. At the same time, the presence of the donor and acceptor units on the same molecule avoids that the chromophore’s performance is affected by its concentration in the medium.$^{129}$ Moreover, Tang et al. showed that, by carefully designing the molecular scaffold, deactivation of the excited state via non-radiative relaxation could be efficiently suppressed, yielding highly efficient TADF emitters.$^{129}$

### 1.3.1.4.1. Multi-resonance emitters

Using a donor-acceptor architecture led to the synthesis of many efficient DA-TADF emitters. However, as mentioned in chapter 1.2.3, this molecular arrangement may display some shortcomings concerning the application of such chromophores in OLEDs. In this context, donor-acceptor chromophores present two main limitations. The first one is the broad emission profile which is often observed when charge-transfer excited states are responsible for the emission. The second drawback is instead related to the inevitable trade-off between large $k_f$ and small $\Delta E_{ST}$. As previously mentioned, both parameters are influenced by the overlap of the frontier orbitals but with opposite effects. The latest investigation of the TADF mechanism showed that it is in principle possible to obtain efficient TADF emitters also with moderately high values $\Delta E_{ST}$ by adjusting the energetic levels of the locally excited states.$^{130}$ However, it requires a great optimization of the molecular structure, and it would be advantageous to optimize the efficiency of the fluorescence emission without affecting other parameters which have a crucial role in the emissive process.
To solve these problems, researchers aimed to find alternative molecular architectures to the twisted DA arrangement. The so-called multi-resonance (MR) emitters are a class of compounds that proved to be a promising alternative. In contrast to the emitters based on a twisted donor-acceptor structure, MR chromophores present a planar and rigid molecular framework and rely on the different resonance of two distinct heteroatoms to achieve a small value for $\Delta E_{ST}$.\cite{21} (Fig. 17), synthesized by Hatakeyama and co-workers, was the first reported example of this kind of emitter.\cite{21} The organoboron compound was initially developed as a host for TADF emitters in OLEDs and is therefore characterized by a highly energetic triplet excited state. The high energy associated with its emission limited its application as a stand-alone chromophore. However, the molecular fragment found additional application as an acceptor fragment in TADF emitters based on D-A architectures (Fig. 16). Nonetheless, the emitter's low value for $\Delta E_{ST}$ of 0.15 eV and relatively high quantum yield of 72% directed the scientific community's attention toward this kind of structural motif.

Since the report of\cite{21}, different examples of MR emitters have been synthesized. The molecules reported so far can be categorized into two classes: boron-nitrogen (22 and 23) or carbonyl-nitrogen MR-emitters (24 and 25 Fig. 17). The two classes' names indicate which heteroatoms or functional groups are included in the molecular scaffold to achieve the multi-resonance effect.

The mechanism through which the MR molecular architecture leads to a TADF emission is exemplified using compound 22 as an example (Fig. 18). Due to the opposite resonance of the heteroatoms present in the molecular scaffold, the excited state undergoes a significant reorganization of the electron distribution, as is highlighted by the pictures of the molecule’s frontier orbitals. The radically different resonance of the HOMO and LUMO in 22 minimizes the exchange energy between the two orbitals, leading to a small $\Delta E_{ST}$. A significant reorganization of the electron density is also observed in DA-TADF emitters; however, in MR-TADF chromophores, this reorganization occurs locally.\cite{132} In these emitters, the two frontier orbitals are not isolated on different portions of the molecules as in DA-emitters, leading to a good overlap between the HOMO and LUMO wavefunctions’ tails and ultimately to a high oscillator...
strength for the fluorescence emission. Additionally, in MR-TADF emitters, the excited state’s vibrational relaxation is hindered thanks to the rigid molecular scaffold and the localization of the frontier orbitals on the atoms rather than along the bonds, leading to a sharp emission profile.\textsuperscript{132, 133}

![Molecular structure and frontier orbitals of 22](image)

**Fig. 18 Molecular structure and frontier orbitals of 22.**

Analogously to DA-TADF emitter, the mechanism of rI\textsuperscript{SC} from in MR-TADF chromophores had been the object of dedicated investigations. Three different mechanisms have been proposed to describe the delayed fluorescence emission of this class of emitters. Specifically, direct conversion of T\textsubscript{1} to S\textsubscript{1}, a rI\textsuperscript{SC} process assisted by mediator triplet states via a vibronic coupling, and a process based on short-range charge-transfer.\textsuperscript{132, 135-137} Even though the emission mechanism of these kinds of chromophores is not entirely elucidated, many efficient MR-TADF emitters have been synthesized since the report of 21 in 2015.\textsuperscript{138} The potential of this class of compounds is highlighted by their remarkable performances when used as emitter in OLEDs. The obtained devices typically showed high EQE and emission with small FWHM. Additionally, modification of the molecular structure had been shown to be helpful to tune some of the emitter’s properties as the emission wavelength and the solution processability.\textsuperscript{139-141}

### 1.3.2. Reference compounds for this work

In this section, some selected TADF emitters are briefly presented. The reported examples are helpful to clarify the background on which the aims of this thesis are developed. The architecture of the two emitters’ classes developed in this work share some strong similarities with the reported examples and aimed to improve some of the aspects of such emitters. The following presented emitters included the series of phenylpyridine-based emitters reported by Wu, Chou, Chi and co-workers (Fig. 19) and ARCSA, reported by Adachi and co-workers (Fig. 20).\textsuperscript{103} In both cases, the chromophores are based on a DA architecture but present some important structural differences.

#### 1.3.2.1. Phenylpyridine-based TADF emitters

The borylated phenylpyridinato fragment and its analogs had been a relevant moiety for the construction of luminescent materials long before the emergence of boron-based TADF emitters. The structural motif had been integrated into the molecular scaffold of a wide number of emitters, and its modification, in particular the extension of its conjugated backbone, proved to be an efficient tool to achieve color tunability of the chromophores’ emission.\textsuperscript{142-147} This molecular fragment was the object of several works performed by the research group of Wang and co-workers who performed a detailed investigation of the photochemical transformations involving this moiety and their mechanism.\textsuperscript{148 149} As reported earlier, the phenylpyridinato boron fragment is a suitable molecular fragment for the construction of acceptor moieties in DA-TADF emitters due to the difference in electronegativity between
the boron and nitrogen atom that induces a greater degree of charge separation in the moiety when compared to the isoelectronic fluorene moiety (see chapter 1.3.1.3.1).\textsuperscript{103, 123}

This section focuses on the TADF emitters developed by Wu, Chou, Chi, and co-workers (Fig. 19) containing a mono- or bi-fluorinated phenylpyridinato boron fragment. The chromophores are based on a DA-architecture in which a boron atom connects the phenylpyridine-based electron accepting moiety to a triphenylamine or carbazole electron-donating fragment. The tetrahedral geometry of the boron atom and the steric repulsion between the substituents ensures the tilted arrangement of the two fragments needed to minimize the overlap of the frontier orbitals. The separation of the frontier orbitals was confirmed by time-dependent density functional (TD-DFT) calculations which showed how the electron density distribution of the LUMO is localized at the fluorinated phenylpyridine fragment of all molecules while the electron density of the HOMO is localized at the triphenylamine or carbazole fragments. In both frontier orbitals, the electron density at the boron center is negligible; therefore, the HOMO-LUMO transition is expected to have a marked charge-transfer character.\textsuperscript{103}

The UV-Vis absorption spectra of the emitters in toluene showed a large extinction coefficient (about 1.5 \cdot 10^4 \text{ M}^{-1}\text{cm}^{-1}) and near independence of the peaks’ position from the polarity of the solvent. This observation led the authors to assume that the observed absorption band can be assigned to a $\pi-\pi^*$ transition. Direct excitation to the charge-transfer excited state is not observed due to the low oscillator strength of the transition induced by the small frontier orbitals’ overlap. All the compounds showed a broad and structureless emission in the visible range with a big Stokes shift. In stark contrast to the absorption spectra, the wavelength associated with the emission maxima was strongly dependent on the solvent polarity. Specifically, a red-shift of the emission was observed in correspondence with an increase in the solvent polarity. These elements confirmed that the emission of the compounds takes place from an excited state with a charge-transfer character. The emission wavelength also proved to be dependent on the kind of donor installed, whereas fluorination of the acceptor did not strongly influence the wavelength of the emission maxima.

The relaxation dynamics revealed that only compounds 26 and 27 emitted via TADF. Under inert conditions, the excited state decays for both triphenylamine derivatives followed a double exponential trend, consisting of a prompt and a delayed decay component. The values of the time constants for the two transients were 77 ns and 2.5 ms for 26 and 75 ns and 2.7 ms for 27. The detected delayed component vanished in the presence of oxygen, thus confirming the involvement of triplet excited states in the emission. The observation of a delayed component sensitive to oxygen and, hence TADF, for only these two compounds of the library, was attributed to the higher $\Delta E_{ST}$ value displayed by the other emitters, which inhibited the rISC process. Interestingly, also compounds 26 and 27 did not show TADF when the measurements were performed in solvents more polar than toluene i.e., DCM or acetonitrile. This behavior can be compared to the one observed by Monkman and co-workers in the case of other TADF.
emitters. The change in medium polarity primarily affects the energy of the charge-transfer excited states, whereas the energy of the locally-excited states is less affected. This leads to a mismatch between the energies of the two different excited states, which ultimately hinders the mediator role of the locally-excited state.

Using 26 and 27 as emitters in OLEDs yielded devices with a remarkable external quantum efficiency of up to 20.2% and 26.6%, respectively. Additionally, the devices based on these two chromophores did not show the fast degradation of the one based on the related boron complex with a non-fluorinated phenylpyridine acceptor unit. These results highlighted the potential of this class of compound as emitters in OLEDs and the beneficial role of fluorination on the stability of the emitters. The effect of the halogens on the properties of TADF emitter and of the devices in which they are employed is treated more in detail in the discussion section of this thesis in chapter 3.4.1.2.3.

1.3.2.2. Photophysical properties of 32

Compound 32 (Fig. 20) had been initially reported by Cheng and co-workers who developed the material as a high energy-gap host material for phosphorescent OLEDs (PHOLEDs). Only later, Adachi and co-workers could show that the compound itself was also an efficient chromophore and that its fluorescence emission displayed a strong TADF component. A more recent work reported by Su and co-workers demonstrated that the whole molecule could also be used as a donor fragment in DA-TADF emitters (see compound 33, Fig. 20). The molecular structure of 32 is also based on a DA structure where the two moieties are tilted one respect to each other. In this case, however, the relative disposition of the two molecular portions is not dictated by steric repulsion but by the rigid arrangement of the spiro motif instead. A spiro structure is constituted by two ring systems that share one single atom. In the case of 32, this atom is represented by the central carbon center, and the two cycles of the spiro system are the central part of the anthrone- and acridine-based fragments which represent the acceptor and the donor portion, respectively.
Fig. 20 Examples of TADF emitters that present one or more spiro centers in their structure.\textsuperscript{89, 151-153}

The geometry induced by the incorporation of the spiro center minimizes the overlap between the frontier orbitals but does not entirely interrupt the communication between the two fragments. As reported by many works, the conjugation of two π systems separated by a spiro center is still active and occurs through what is indicated as spiro conjugation.\textsuperscript{154-158}

The implementation of the spiro architecture in organic molecules has a relevant role in the synthesis of materials for organic optoelectronic applications and is not restricted to the synthesis of DA emitters.\textsuperscript{159, 160} Including a spiro center in the molecular scaffold usually leads to an increase in the glass transition temperature (T\textsubscript{g}) of the material and an increase in the steric demand of the molecular structure. These two characteristics are generally considered beneficial for molecules that aim to be utilized in optoelectronic devices. A high value of T\textsubscript{g} implies a high stability of the material’s amorphous state.\textsuperscript{161, 162} Highly amorphous materials are particularly suitable for optoelectronic applications since the boundaries between microcrystallites in crystalline materials act as traps for charge carriers, thereby contributing to the device degradation.\textsuperscript{163, 164} A higher steric bulk around the molecular scaffold, on the other hand, protects the molecules’ orbitals and disfavors the compound’s participation in intermolecular processes. This strategy is particularly suitable for suppressing exciplex formation or deactivation of the excited state via triplet-triplet annihilation. The benefits of the steric protection offered by the rigid spiro fragment are highlighted by the analysis of the photophysical properties of compound 35 (Fig. 20), reported by Zhang and Wang. The authors demonstrated how the introduction of the spiro moieties efficiently shields the frontier orbitals of 35 and protects the excited states of the emitter from concentration quenching.\textsuperscript{89} The rigid framework of the spiro moiety also lends more rigidity to the molecular scaffold, which is beneficial for suppressing molecular vibration and, therefore, non-radiative deactivation. It also suppresses molecular reorganization upon excitation, thereby inducing narrower emission and higher color purity. The higher rigidity of the spiro fragment was indicated as the cause for the high fluorescence rate and thermal stability of compound 34 (Fig. 20) reported by Liao, Jiang and co-workers.\textsuperscript{153}
The investigation of the photophysical and electronic properties of 32 delivered a picture that is similar to the one reported for compound 1 (Fig. 11) and the emitters developed by Wu, Chou Chi, and co-workers (Fig. 19).\textsuperscript{32, 103} Calculation of the HOMO and LUMO highlighted their strong localization on the donor and acceptor moiety, respectively. Thanks to the adoption of the DA architecture, the lowest excited state is characterized by a strong charge-transfer character, as suggested by the dependence of the emission wavelength from the polarity of the solvent employed in the measurements. The low overlap between HOMO and LUMO induced by the spiro moiety led to a small value for \( \Delta E_{ST} \), estimated to be 0.03 eV from the measurements in toluene solution. Thanks to the low energy difference between the singlet and triplet manifolds, the chromophore displayed an efficient TADF emission, as confirmed by the transient decay measurements in the presence and absence of oxygen. The presence of oxygen also strongly influenced the photoluminescence quantum yield of the emitter that, when measured in toluene, improved from 4% to 70% upon argon purging. The photoluminescence quantum yield of a 20% 32:DPEPO thin film showed an even higher PLQY of 81%. An efficient OLED with 16% external quantum efficiency was obtained by using 32 as the emitter, confirming the active harvesting of triplet excited states via TADF.

The emission mechanism of 32 was investigated in two different publications. Marian and co-workers used a computational approach to dissect the various stages of the chromophore’s emission and pinpoint the different excited states involved in the TADF process. In contrast, Monkman and co-workers analyzed the emitter utilizing different spectroscopic techniques as steady-state fluorescence spectroscopy, time-resolved emission spectroscopy, and transient emission spectroscopy.\textsuperscript{84, 165} The investigations of both research groups led to a similar description of the emission process and highlighted how employing a simple molecular architecture does not inherently translate in simple photophysical properties.

Thanks to their investigations, the authors could identify the connection between four different excited states of the emitter and the recorded emissions. Involved in the detected emission are an excited state localized on the donor (\( LE_D \pi\pi^* \)), two different excited states localized on the acceptor (\( LE_A n\pi^* \) and \( LE_A \pi\pi^* \)), and one charge-transfer excited state (CT). (The hyphenated prefix in the notation used in the following description indicates the multiplicity of the indicated state).

The emission profile of the chromophore varied if the wavelength of the light used for the excitation changed. Specifically, using a light source with an associated wavelength of 330 nm or 350 nm yielded two different emissions profiles, each containing two different peaks. The two multi-peak spectra shared the same CT emission, whereas the other two peaks were assigned to emission from two excited states, namely, \( 1LE_A n\pi^* \) and \( 1LE_D \pi\pi^* \). This observation was also confirmed by the excitation measurements where the high-energy \( 1LE_D \) excited state gave rise to emission from three different singlet states.
simultaneously: $^1\text{LE}_D \pi\pi^*$, $^3\text{LE}_A \pi\pi^*$, and $^1\text{CT}$. This behavior renders 32 a doubly anti-Kasha emitter which is a rarely encountered case. 32 displayed an anti-Kasha behavior also in the phosphorescence spectra recorded at low temperature. Under these conditions, emission from both triplet excited states $^3\text{LE}_A \pi\pi^*$ and $^3\text{LE}_D \pi\pi^*$ could be detected.

The presence of oxygen did not entirely quench the charge-transfer emission. Therefore, the authors could conclude that the CT state can also be generated upon electron transfer from the high energetic locally-excited state centered on the donor moiety ($^1\text{LE} \pi\pi^*$) or by direct excitation when the excitation wavelength was lower than 380 nm. Also, the wavelength of the CT emission does not change significantly during the emission, suggesting that the rigid spiro structure restrains the vibrational relaxation of the excited state. Removing the oxygen resulted in a great increase in the CT emission’s intensity, indicating a significant contribution of triplet excited states to the delayed component.

Investigation of the TADF mechanism showed that the LE$_A$ ππ* state has a critical role in the delayed fluorescence emission process. $^3\text{LE}_A \pi\pi^*$ couples nonadiabatically to the $^3\text{CT}$ state mediating reverse intersystem crossing to $^1\text{CT}$, thereby allowing the delayed fluorescence. Due to the different influence of the solvent polarity on LE and CT states, the relative energy difference between these excited states could be altered by modifying the solvent employed. In methylcyclohexane (MCH), $^3\text{LE}_A \pi\pi^*$ and $^3\text{CT}$ are energetically close, promoting the rISC process with its rate reaching $10^7$ s$^{-1}$. However, in these solvents, the efficiency of the delayed fluorescence is lower when compared to the one recorded in toluene and DCM. The author attributed the observed behavior to the presence of competing decay channels in the triplet manifold which hinder that all the excitons reach the TADF-active excited state.
2. Aim of the work

The aim of this thesis is the development of two novel classes of boron-based spiro compounds and the investigation of their performances as emitters exhibiting thermally activated delayed fluorescence (TADF). Examples for the two proposed series of compounds are depicted in Fig. 22. Both structures share a common donor-spiro-acceptor architecture where a spiro atom connects a bidentate electron-donating moiety to an electron-withdrawing one.

![Fig. 22 Examples of the two categories of compounds covered in this work and summary of their common structural characteristics.](image)

The donor-spiro-acceptor arrangement keeps the two fragments perpendicularly aligned, one with respect to the other, while still allowing their conjugation. This structural motif has been shown to directly impact the molecular orbitals’ properties of the emitters. The HOMO and LUMO are highly localized at the donor and acceptor, respectively, and the overlap between the two frontier orbitals is minimized due to the perpendicular arrangement. According to the numerous reported examples, these conditions should also lead to a small energy difference between the singlet and triplet excited states ($\Delta E_{ST}$), which is a key prerequisite to obtain efficient TADF emitters. The adoption of a spiro-based architecture has been also shown to positively affect other physical properties connected to the chromophore applications. Specifically, the spiro motif generally yields more rigid structures that minimize molecular vibrations, thus minimizing non-radiative deactivation of excited states. The twisted structure reduces also molecular aggregation, which has a direct effect in suppressing intermolecular fluorescence quenching. At a bulk level, the introduction of a spiro center in the molecular structure can be used to decrease the decomposition and increase the glass-transition temperatures ($T_d$ and $T_g$).\textsuperscript{166-171}

The two targeted classes of compounds share the same structural arrangement, but they differ with respect to the coordination number of the boron atom and its position in the molecular backbone. In the context of this work, the two classes will be named \textbf{spiro-B} and \textbf{spiro-C}. In the first class, the boron atom is tetracoordinated and found at the spiro center, whereas in the latter class, \textbf{spiro-C}, the spiro center is
constituted by a carbon atom, and a tricoordinated boron atom is found at the acceptor moiety. The structural differences between the two families of compounds greatly influence the design of the synthesis paths. For this reason, the development of the synthesis sequences will be discussed separately.

2.1. spiro-B

The boron atom in the molecules belonging to the class spiro-B plays an important structural role since its stable coordination to the nitrogen atom is what enables the constitution of the spiro center. The phenylpyridine borane fragment (ppyB) is isoelectronic to the fluorene fragment but has a higher degree of charge separation, which makes the boron-based moiety more suitable for the construction of TADF molecules. As previously shown by Shiu, Chen et al., this fragment can be successfully employed in the synthesis of TADF emitters (chapter 36.1.3.2.1). In the wake of the findings published by Shiu, Chen et al., one of the aims of this work is to test whether the use of a bidentate donor moiety introduces a change in the photophysical properties of the emitters. In particular, we were interested in testing whether the introduction of a spiro center would increase the rigidity of the system suppressing the non-radiative decay of the excited state, and thus increase the efficiency of the radiative processes.

Fig. 23 Comparison between the structures of the phenylpyridine-borane based TADF emitters synthesized by Shiu, Chen et al. (compounds 26, 27, 28, 29, 30, and 31), and one of the target molecules of this work, compound 36.

Preliminary DFT calculations confirmed that the change in the molecular geometry should not interfere with the spatial distribution and separation of the frontier orbitals. As confirmed by the representation in Fig. 24, the HOMO and the LUMO are still expected to display a high localization at the donor and acceptor moiety, respectively.
Our goal was to first establish a synthesis route towards this class of compounds and, subsequently, expand the number of available emitters by modifying the synthesis process. To gain access to a broader series of molecules, we intended to apply two different strategies. The first one implied the differentiation of the donor and acceptor moieties by employing different building blocks to synthesize the luminophore itself. The second approach revolved around the development of a downstream derivatization protocol to be applied to an already isolated emitter. Both approaches were analyzed in the context of this work since they both present peculiar advantages. In the first strategy, the already optimized synthesis sequences can be applied using different acceptor or donor fragments without the need to establish new synthesis steps. On the other hand, by following the second approach, it is possible to introduce functional groups that are not tolerated by the conditions for the synthesis of the parent emitter.

In molecules with a donor-acceptor architecture, the relative strengths of the donor and the acceptor units directly influence the HOMO-LUMO energy difference, which, in turn, determines the emission wavelength of the chromophore. Variations in the molecular backbone would therefore enable us to tune the emission wavelength of the materials. Alterations of the donor or the acceptor fragments could also modify the rates of the different photochemical processes in which the excited state is involved. Therefore, we intended to analyze the influence of the above-mentioned structural changes on the excited-state lifetime and the TADF performances of the emitters. We hypothesize that changing the heteroatom present at the donor moiety or adding a heavy atom at the same fragment should alter in a considerable manner the lifetimes of the excited states. In accordance with reported examples, these modifications have a direct influence on the spin-orbit-coupling, and therefore directly influence the intersystem crossing (ISC) and reverse intersystem crossing (rISC) rates. For instance, it has been reported that the incorporation of a sulfur atom facilitates the intersystem crossing (ISC) between singlet and triplet excited state. This change resulted in either a boost of the TADF performance or the emission of light via room temperature phosphorescence (RTP). In another example reported by Winter and co-workers, the introduction of a platinum atom was used for the synthesis of hybrid BODIPY-platinum complexes that can display both fluorescence and phosphorescence emission.\textsuperscript{172-174}

As mentioned earlier, the possibility of tuning the emission wavelength of the fluorophores is particularly desirable for the applications in which the emitter is employed. For instance, in OLED displays, different emitters with different emission wavelengths are needed. Having a method to influence and regulate the rates of the processes in which the excited state is involved also offers great advantages. It could be used to increase the rISC rate which, in TADF emitters, results in a shorter triplet excited-state lifetime and in an overall increase of the efficiency. On the other hand, the extension of the excited-state
lifetime is of interest for the generation of emitters with a persistent luminescence or in the field of organo-catalysis.

Lastly, we intended to apply the downstream derivatization protocol for the synthesis of more peculiar emitters, namely enantiopure chiral chromophores. More specifically, we intended to introduce a chiral center in correspondence of the tetracoordinated boron atom by means of derivatization of the donor fragment. We expected that combining the intrinsic asymmetry of the phenylpyridine-based acceptor moiety with a selective derivatization at one aromatic ring of the donor would grant a relatively straightforward access to this class of compounds. Due to the stability of the tetracoordinated coordination at the boron atom, such compounds should also retain their stereo configuration and not be subject to racemization, giving therefore access to stable chiral emitters. Chiral fluorophores are relevant for their circularly polarized emission, which finds many applications ranging from display devices, circularly polarized luminescence (CPL) lasers and biological probes.\textsuperscript{175-182}

2.2. \textit{Spiro-C}

In the \textit{spiro-C} class, the spiro center is constituted by a carbon atom, and, in contrast to the class \textit{spiro-B}, the boron atom is tricoordinate and found at the acceptor moiety. The structural role of the boron atom is to bridge the two aromatic rings of the acceptor moiety, which ensures the formation of one of the two rings at the spiro center. However, the structural function of the boron center is only secondary to its fundamental role of determining the molecule’s electronic properties. The boron atom is \textit{sp}\textsuperscript{3} hybridized and has, therefore, an empty \textit{p} orbital, which confers an intrinsic electron-accepting nature to the atom. The presence of the tricoordinated boron center is what ultimately confers the electron accepting nature to the fragment.

![Fig. 25 General structure of the compounds belonging to the spiro-C class compared with 32, synthesized by Adachi and co-workers.](image)

This class of compounds is strongly related to 32, synthesized by Adachi and co-workers in 2013.\textsuperscript{151} The two compounds share the same structural characteristics, except for the functional group characterizing the acceptor moiety. Specifically, in 32, a carbonyl group is in place of the aryl borane fragment found in compound 37-R. As previously mentioned, the spiro-based architecture of 32 proved to be efficient in creating the already mentioned prerequisites for TADF to take place. In this compound, the HOMO and the LUMO are spatially separated and localized on the donor and acceptor moieties respectively (Fig. 21). The luminescence of compound 32 originates from a charge transfer excited state, and the energy of the singlet and the triplet excited state differs only by 0.03 eV. When implemented in
an OLED device, compound 32 showed to be an efficient TADF emitter with a photoluminescent efficiency of 81% and a relatively high external quantum efficiency of 16.5%.

With the synthesis of compounds having the general formula 37-R, this work aimed to develop a series of emitters that would retain the remarkable photophysical characteristic of 32 but at the same time be more versatile. We expected that being able to modify the third substituent R at the boron center would enable us to tune the photophysical properties of the emitter in a fast and practical manner. Analogously to the considerations presented for class spiro-B, using substituents with different electronic properties should modify the strength of the acceptor, therefore the HOMO-LUMO energy difference, and ultimately the emission wavelength. We regarded this additional feature as a major improvement for this kind of emitter with respect to 32, since, as mentioned in the previous paragraph, achieving such a degree of flexibility is particularly advantageous for molecules intended to be used in the field of OLED.

Rather than combining different boron-based starting materials with the donor moiety, we aimed to design a synthesis pathway that would give access to a common donor-spiro-acceptor precursor. This parent compound could then be functionalized with different substituents during the last stage of the synthetic pathway. We believed that this approach would allow us to simplify the access to several members of this compound class and would enable the introduction of functional groups that are not compatible with the synthesis conditions of the main scaffold.
3. Spiro-B Emitters

3.1. Synthesis

The synthesis approaches, which had been investigated in this work, are exemplified in Fig. 26 using compound 36 as an example. Firstly, the aryl pyridine scaffold is borylated by means of an electrophilic aromatic borylation, yielding the intermediate 38-X. We found compound 38-X to be a versatile intermediate in the synthesis of this class of molecules since its boron center is moisture and air stable due to its tetracoordinated state. At the same time however, the two halogen substituents are reactive enough to allow further functionalization.

In the second step, the installation of the donor moiety takes place, and two different reactions were tested at this stage. The first one being the direct addition of a twofold metalated species 39-M to the borylated phenylpyridine 38-X (Path A), and the second one the Lewis acid-promoted arylation protocol with silanes or stannanes 40-Si or 40-Sn, respectively (Path B).

An alternative synthesis approach to this class of compounds is depicted in Fig. 27. This particular reaction sequence was used for the synthesis of the first compounds displaying a 2'-borylated 2-phenylpyridine unit, reported in 2008 by Wang and coworkers. The synthesis approach implies the reaction between a metalated phenylpyridine fragment and a boron halide precursor and had been broadly and successfully applied by the same research group in the synthesis of many analogue compounds. It differs from Path A (Fig. 26) for the fact that the boron atom of the borylated starting material is tricoordinated and is not connected to the phenylpyridine fragment.
Fig. 27 Alternative synthesis approach towards the spiro-8 class of compounds. This reaction was used by Wang and coworkers for the synthesis of the first compound with a 2'-borylated phenylpyridine unit 41.

Compared to Path A, the one reported by Wang and co-workers presents mainly two critical points. Firstly, it requires a brominated aryl pyridine scaffold, which may not be easily accessible, especially in the case of more complex 2-arylpyridines and related derivatives. Secondly, the boron-based electrophiles are often unstable, or their synthesis may require many steps. For the above-mentioned reasons, we therefore decided to exclude this synthesis approach from our investigation.

3.1.1. Direct electrophilic aromatic borylation

The direct and regioselective borylation of 2-arylpyridines was firstly reported in 2010 by the group of Murakami and coworkers. In their publication, they presented a novel procedure for the direct regioselective borylation of 2-arylpyridines (Fig. 28a) that allows the 2’-position to be selectively functionalized without the need of a previous derivatization. The reaction protocol is extremely straightforward and involves the addition of an excess of boron tribromide to the phenylpyridine-based substrate in the presence of a non-coordinating base, e.g. DIPEA. The regioselectivity of this reaction relies on the directing effect of the nitrogen that coordinates one molecule of boron tribromide in the first step of the mechanism. Subsequently, the abstraction of a bromide substituent from the coordinated boron tribromide by another molecule of BBr$_3$ generates a borenium cation. Once this active species is generated, electrophilic attack at the phenyl ring at the 2’ position occurs. The proton at that position is then scavenged by the base, restoring the aromaticity of the system.

![Protocol for direct borylation](image)

Fig. 28 Protocols for the direct borylation phenylpyridine and its derivatives a) developed by Murakami and coworkers b) developed by Ingleson and coworkers.

A similar borylation protocol was reported later by Ingleson and coworkers (Fig. 28b). It differs from the first reported reaction in that BCl$_3$ is used as the borylating agent, 2,4,6-tri-tert-butylpyridine as the base and AlCl$_3$ is additionally required. In this reaction, AlCl$_3$ plays an essential role in the generation of the borenium cation. The extraction of a chloride from a coordinated BCl$_3$ cannot be performed by a second molecule of BCl$_3$ due to its lower Lewis acidity compared to the one of BBr$_3$ and is therefore carried out by AlCl$_3$. BCl$_3$ is a milder reagent compared to BBr$_3$, which simplifies its handling and generally possesses a lower price than boron tribromide. However, we chose to apply the procedure reported by
Murakami and coworkers, since the base employed by Ingleson and co-workers has generally a much higher price than N,N-diisopropylethylamine and, in our hands, the procedure with boron tribromide delivered higher yields. As illustrated in chapter 3.1.2.1, both borylated materials showed comparable reactivities and results in the next synthesis step.

3.1.1.1. Synthesis of the borylated precursors

The above-mentioned borylation procedures are not limited to phenylpyridine and in the literature many examples containing the same sub-structural moiety had been reported. In addition to 38-Br, we applied the borylation protocol established by Murakami and co-workers to reproduce the synthesis of compounds 42 and 43. The obtained molecules were characterized by means of NMR spectroscopy and the obtained \(^1\)H, \(^{13}\)C and \(^{11}\)B NMR spectra corresponded to the one reported in the literature. Additionally, two new compounds could be synthesized by applying the same borylation protocol using benzo[h]quinoline and 2-phenylbenzo[g]quinoline as the starting materials. The new borylated precursors 44 and 45 were obtained in 55% and 89% yield, respectively, and were characterized by means of NMR spectroscopy and elemental analysis. The signals recorded in the \(^1\)H and \(^{13}\)C NMR spectra were in line with the expected pattern for the two structures. In the \(^{11}\)B NMR spectra one single signal was observed at \(-0.51\) ppm and \(-1.65\) ppm for compound 44 and 45, respectively. The observed shifts were in line with the one observed for the already reported borylated compounds and therefore confirmed the successful introduction of a tetracoordinated boron atom with two bromide substituents in the molecular backbone. In addition, the solid-state structures of compounds 43 and 44 could be also obtained which further confirmed the obtainment of the desired compounds.

The four different borylated compounds 42, 43, 44 and 45, Fig. 29, generate a small library of precursors that can be used to generate chromophores with different accepting moieties. With the obtained molecules we could examine the effect of the fluorination of the acceptor, extension of its conjugated \(\pi\) system and the influence of the position of the additional aromatic ring on the photophysical properties of the chromophores.

![Fig. 29 Additional borylated intermediates synthesized via a protocol of Murakami and co-workers.](image)

3.1.2. \(\text{AlCl}_3\) catalysed desilylation/ destannilation

The use of aryllithium or aryl Grignard reagents for the derivatization of tricoordinated boranes is an established and often applied procedure.\(^{187, 188}\) A similar approach was also chosen in the above-mentioned work of Shiu, Chen et al., for the derivatization of the tetracoordinated phenylpyridine borane fragment.\(^{103, 188}\) However, when aryllithium or aryl Grignard reagents are used in combination with tetracoordinated borane adduct substrates, the targeted compounds are normally obtained in mediocre yields. The outcome of the reaction can sometimes be improved by using aluminum or zinc reagents
which, however, may not always be easily accessible.\textsuperscript{189} We, therefore, looked for alternative reactions that would not present the above-mentioned critical points and that could deliver the desired compounds in higher yields.

Indeed, Ingleson and co-workers had reported a novel method for the functionalization of tetracoordinated borane adducts, which aimed to address the above-mentioned problems. They looked for a derivatization procedure that could be applied in non-ethereal solvents and that would make use of easily accessible reagents which are not susceptible to hydrolysis. The developed method involves a boron-desilylation or -destannylation reaction catalyzed by aluminum trichloride (Fig. 30).

![Fig. 30 Specific example of the application of the boron-desilylation protocol developed by Ingleson and co-workers.](image)

This synthesis method is strongly connected to the boron-silicon or boron-tin exchange reaction, traditionally used for the synthesis and derivatization of tricoordinated boranes. The combination of a tetracoordinated borane adduct and an organo-silicon or organo-tin reagent, however, does not lead to any reaction, since the Lewis acidity of the boron center is quenched by the coordination of the fourth substituent, i.e., the base. For this reason, in Ingleson’s protocol, a catalytic amount of AlCl\textsubscript{3} is employed. The mechanism of the reaction is schematized in Fig. 31. Aluminum trichloride initiates the reaction by acting as a Lewis acid and extracting a chloride ion from the borylated phenyl pyridine fragment. The in-situ generated borenium ion is then able to react in a transmetalation reaction with the aryl silane or stannane precursor. The byproduct of the transmetalation reaction starts another reaction cycle by acting as the halide extracting agent thus generate the borenium cation. AlCl\textsubscript{3} can therefore be used in a catalytic fashion.

![Fig. 31 Schematic representation of the reaction mechanism for the AlCl\textsubscript{3} catalyzed desilylation/ destannylation reaction reported by Ingleson and co-workers.](image)
3.1.2.1. Optimization of the reaction conditions

The synthetic method was adapted to our system and the reaction conditions were optimized in the synthesis of compound 36. As reported by Ingleson and co-workers, this protocol is effective with both organo silanes and organo stannanes. Aryl silanes have the advantages of being more stable and less toxic than the corresponding stannanes, it is therefore preferred to employ such derivatives when possible. For this reason, we firstly tested the reactivity of the aryl silane 40-Si towards the two borylated precursors 38-Cl and 38-Br, as depicted in Fig. 32.

![Fig. 32](image)

Under the conditions published by Ingleson and co-workers, the reactions between the silylated precursors 40-Si and the borylated phenylpyridines 38-Cl or 38-Br deliver no desired product (38-Cl) or only traces of it (38-Br).

The reaction was performed in 1,2-dichlorobenzene at 60 °C with a reaction time of 16 h. For compound 38-Cl no reaction could be observed, whereas for 38-Br, at least traces of the starting material were converted to 36. Thus, 40-Si was replaced by the more reactive tin analogue 40-Sn, and the reaction was carried out under similar conditions (Fig. 34).

![Fig. 34](image)

The boron-destannylation reaction successfully yields product 36 when either 38-Cl or 38-Br are used as reaction partners together with 40-Sn.

Both compounds 38-Cl and 38-Br lead to the formation of the desired product. The reaction proceeds smoothly towards compound 36 and delivers a clean crude mixture (Fig. 35). Both compounds 38-Cl and 38-Br delivered comparable results in terms of the purity of the crude material delivered by the reaction. We therefore decided to use compound 38-Br for this synthesis (obtaining compound 36 in 51% yield) and for the following experiments. As mentioned above, the borylation reaction to 38-Br makes use of cheaper base and in our hands delivered the borylated product in higher yields.

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51
3.1.2.2. Variation of the tin precursor

In order to investigate the effect of the electron donor unit on the photophysical properties of the target compounds, we proceeded by testing two additional stannanes, 48 and 49, under the same conditions described in the previous chapter to obtain compounds 50 and 51, respectively (Fig. 36).

Fig. 35 Comparison of the $^1$H NMR spectra (aryl region only) of the crude reaction mixture delivered by the boron-destannylation reaction (spectrum 1) and the purified compound 36 (spectrum 2). The solvent signal is marked with the symbol *.

Fig. 36 The boron-destannylation reaction could also be successfully employed for the synthesis of 51, but failed in delivering compound 50.
While using 49 the reaction delivered the desired product 51 in 72% yield, in the case of 48 a complex mixture was obtained. Further experiments revealed that compound 48 is not stable in the presence of AlCl₃ and quickly undergoes decomposition at room temperature. The products of the decomposition reaction were not isolated, but the reaction was monitored in situ using NMR spectroscopy (Fig. 37). The peak labeled with “1” corresponds to the methyl substituents connected to the tin atom whereas peaks 2 and 3 can be assigned to the tert-butyl groups. As expected, the integral ratio equals to 6:9:18. It has been shown previously that tert-butyl groups attached to an aromatic ring can be cleaved in the presence of AlCl₃.¹⁹⁰ This had been exploited in some synthesis sequences to make use of such substituents as removable directing group.¹⁹⁰ Although this reaction may be one of the possible decomposition pathways, the disappearance of peak 1 indicates that also the tin-bound methyl groups are affected.

![Fig. 37 Comparison between the ¹H NMR spectra of compound 48 before (spectrum 1) and after (spectrum 2) addition of AlCl₃. The solvent signal is marked with the symbol *.

3.1.2.3. Variation of the borylated precursor

In analogy to the previous chapter, we then proceeded to increase the number of compounds in our library by using the additional borylated precursors, which were described in chapter 3.1.1.1. Employing the partially fluorinated precursor 42 in the established boro-destannylation protocol, successfully led to the synthesis of compound 52 in 30% yield (Fig. 38).
Fig. 38 Extention of the compound library can be achieved by using the partially fluorinated precursor 42.

Under the same conditions, the reaction with the borylated precursors 43, 44 and 45 only delivered traces of the desired products. Thus, higher reaction temperatures or longer reaction times were needed for the reactions to reach completion. In analogy to the original reaction conditions published by Ingleson and co-workers (Fig. 30), low-boiling DCM was replaced by 1,2-dichlorobenzene to allow a safe conduction of the reaction at higher temperatures. The reaction was then carried out at 60°C and was complete within 24-48 h depending on the reactants (Fig. 39).

Fig. 39 Adapted reaction condition for the boron-destannylation reaction when precursors 43, 44 and 45 are used.

The newly established conditions were used to combine the borylated precursors 43, 44 and 45 with both tin compounds 40-Sn and 49 yielding the compound listed in Fig. 40 with their respective yields.

Fig. 40 Boron-based donor-spiro-acceptor compounds with extended π systems at the electron acceptor.
3.1.3. Derivatization of borylated aryl pyridines via direct addition of nucleophile

The double methylation at the boron atom of the phenylpyridine dibromo borane fragment $38$-$\text{Br}$ by direct reaction with trimethylaluminum is commonly used to convert the bromo substituents into more inert methyl groups generating a much more stable compound with a higher solubility in common organic solvents. This kind of derivatization is often performed in syntheses where the incorporation of the borylated fragment in the molecular structure has a core importance, whereas the substituents at the boron have a secondary role.\textsuperscript{145, 191, 192}

The methylation and more generally, the alkylation of this kind of substrates can be achieved in high yields using different trialkyl aluminum or dialkyl zinc nucleophiles. In contrast, installation of aryl substituents by direct reaction with a nucleophile is often characterized by medium or low yields. Even though Murakami and co-workers showed that the reaction between triphenylaluminium and $38$-$\text{Br}$ can deliver the diphenylated product in high yield, this transformation had not been applied in other works. Diaryl zinc and Grignard reagents are instead the electrophiles of choice to obtain the diarylated products. Other employed electrophiles include aryllithium and arylcopper reagents. However, the first ones usually deliver particularly low yields, and the latter was only used in the case of $\text{Cu(C}_6\text{F}_5\text{)}$.\textsuperscript{146, 183}

These general considerations were found to be true when some of the above-mentioned reactants were used for the synthesis of the compounds object of this chapter. We firstly investigated the arylation of the borylated phenyl pyridine $38$-$\text{Br}$ using the lithiated species $39$-$\text{Li}$. This dilithiated species can readily be synthesized from unsubstituted $N$-methyldiphenylamine with $^n\text{BuLi}$, thanks to the ortho-directing effect of the nitrogen atom. Direct addition of $39$-$\text{Li}$ to $38$-$\text{Br}$ in THF (Fig. 41) yielded a complex mixture, where the product was present but in minor traces (Fig. 42). Performing the reaction in benzene improved the quality of the crude mixture dramatically and using the arylzinc derivative $39$-$\text{ZnCl}$ did not produce the broad NMR resonances in the range between 6.4 and 6.7 ppm of the previous experiments but other unknown impurities with well-defined signals.

![Fig. 41 General reaction scheme for the synthesis of compound 36 via direct addition of an arylzinc or -lithium reagent to compound 38-Br.](image)
Fig. 42 Comparison between $^1$H NMR spectra (only aromatic region) of pure compound 36 (spectrum 1) and different crude mixtures obtained by the direct addition of a nucleophile to 38-Br. Spectrum 2: addition of 39-ZnCl to 38-Br in THF; Spectrum 3: addition of 39-Li to 38-Br in THF; Spectrum 4: addition of 39-Li to 38-Br in THF. The solvent signal is marked with the symbol ⚫.

For the synthesis of compound 36, this method showed to be inferior compared to the boro-destannylation protocol illustrated in the previous chapter. However, we believed that this synthesis strategy could still be a valid alternative to produce compound 50, where the AlCl$_3$ catalytic destannylation failed. The use of aryllithium reagents in the reaction was excluded due to the particularly poor results obtained in the synthesis of 36. We therefore aimed to the generation of an arylzinc or arylmagnesium nucleophile starting from the brominated compound 58. The synthesis of the Grignard reagent from 58 failed using Mg turnings. Surprisingly, the reaction did not proceed also when the more reactive magnesium powder or isopropylmagnesium chloride were used. To generate the arylmagnesium or arylzinc derivative of compound 58, a lithiation-transmetalation sequence was applied. Firstly, the lithiation of the brominated substrate was performed using nBuLi followed by a transmetalation reaction with MgBr$_2$ or ZnCl$_2$, respectively. The two metalated intermediates could then be tested in the reaction with compound 38-Br. The Grignard reagent delivered the less complex crude mixture and was therefore used for the final synthesis of 50 delivering the product in 33% yield.

Conducting the reaction directly with the aryllithium compound in a non-ethereal solvent (e.g. benzene) could be another way to improve the yield of this transformation. However, the optimization of this reaction was not the focus of this work and further experiments were not conducted.
Fig. 43 Reaction procedure adopted for the synthesis of compound 50
3.1.4. Compounds library

Thanks to the modular synthesis approach reported in the previous chapters a library of 9 novel compounds was constructed (Fig. 44).

The new compounds were primarily characterized by means of NMR spectroscopy and elemental analysis, and the outcome of the measurements was in accordance with the expected structure. For the donor-acceptor chromophores, the sets of signals belonging to the donor and the acceptor moieties could be clearly identified, and their relative integrals confirmed the presence of an equal number of the two
moieties in the structures. In all the $^{11}$B NMR spectra, only one signal could be observed, confirming the presence of a single type of boron center in the molecular backbone. The recorded shift for the $^{11}$B nuclei typically lied between 0 and 0.68 ppm except for compounds 53 and 55, for which the values of 2.96 and 3.57 ppm were obtained, respectively. Nonetheless, the recorded shifts are in agreement with the one reported for similar compounds with a tetracoordinated boron center and a chelating substituent based on a phenylpyridine moiety. All the compounds could be analyzed under normal atmospheric conditions without the need of employing dry solvents, and no worsening of the NMR spectra was observed within 24 h from the preparation of the solution. This behavior confirmed the expected stability of the compounds conferred by the formation of the Lewis acid-Lewis base adduct between the nitrogen and the boron atom. Nonetheless, it must be noted that a dark blue precipitate slowly formed in the aging solution of emitters based on the diphenyl methyl amine donor. The precipitate proved to be an extremely insoluble material, and no hints about its composition could be gained.

Additionally, the solid-state structure of all the newly synthesized molecules was provided by X-ray diffraction analysis of suitable single crystals. The outcome of these analyses provided further confirmation that the target molecules had the expected structure. The most important aspects and parameters of the compounds’ solid-state structures are discussed in chapter 3.3, whereas the photophysical properties of the emitters are the object of chapter 3.4.
3.2. Downstream functionalization and synthesis of chiral emitters

After the successful generation of nine different donor-spiro-acceptor molecules by combining different donor and acceptor moieties, we set out to develop a complementary strategy to extend the library of these compounds. Therefore, we investigated the derivatization of the materials in the last synthesis step with a focus on the modification of the chromophore’s donor moiety. We considered this different approach towards new members of the spiro-B class to be particularly appealing for mainly two reasons. Firstly, it would furnish an additional tool to modify the HOMO and LUMO energies of the emitters, hence their photophysical properties, without the need to synthesize different starting materials for the synthesis of the emitter itself. Secondly, it could be used to obtain emitters with more sophisticated structures or with functional groups that are not compatible with the synthesis of the parent compounds. The introduction of a substituent at only one of the two aromatic rings of the donor fragment would introduce a stereocenter at the tetracoordinated boron atom and therefore provides access to chiral luminophores.

The high stability against hydrolysis displayed by this class of compounds is connected to a strong coordination of the nitrogen atom to the boron center. This characteristic made us confident that these compounds could be exposed to different reaction conditions without compromising the integrity of the spiro center. We also expected that the energy barrier for a racemization would be sufficiently high since the inversion of the boron center would require the temporary cleavage of the B-N bond. Derivatization of the acceptor moiety may have delivered analogous tuning possibilities of the HOMO-LUMO energy gap, however, it would have not reduced the symmetry of the molecule and no stereocenter would have been introduced at the boron atom. For this reason, the derivatization of the donor moiety was prioritized and investigated in the context of this work.

Even though some experiments conducted using compounds 36 and 51 are commented, we have mainly focused our attention on the derivatization of compound 56. This compound showed a long-term stability in solution which gave us more freedom in terms of the reaction conditions and purification methods that could be employed. Moreover, we expected that the lower symmetry of the acceptor unit, with regard to its molecular shape, would be advantageous to induce certain photophysical effects due to the chirality.

The strategy employed for the functionalization of the donor moiety of compound 56 and the generation of chiral emitters had been divided in three steps (Fig. 45).
Fig. 45 Schematic representation of the synthesis strategy employed for the derivatization of compound 56.

The first stage consisted in the mono halogenation of the chromophore donor moiety. This initial step would already generate a pair of enantiomers, but it had mainly the purpose of introducing a reactive functional group without altering the electronic properties largely. The presence of a halogen substituent would create many possibilities for further functionalization of the fragment via a wide variety of transformation. We especially aim to the application of transition-metal catalyzed reactions which are normally characterized by mild reaction conditions.

In the second step, the two enantiomers are converted into diastereomers, which are then separated. To achieve this, we introduced an enantiomerically pure chiral residue. The choice of the chiral residue was driven by the ease of separation of the two obtained diastereomers and if further transformations could be performed using the introduced substituent.

The third and last stage consisted in the conversion of the isolated diastereomers in enantiomers taking advantage of the functional group introduced in the previous step. To obtain a couple of enantiomers, the chiral substituent had to be modified in such a way that it loses its chirality.

The investigation of this approach is illustrated in detail in the next chapters. The best methods found for the mono-halogenation of the donor moiety, the derivatization with chiral residues and the separation of the stereoisomers are highlighted. As a proof of concept, the further transformation of the obtained diastereomers was tested for one example and numerous other alternatives can be envisaged, which would, however go beyond the scope of this thesis. In the next chapters, when a one or more stereogenic centers are present in the molecular structure, the following naming rules are adopted. The suffix “En-” is added to the compound number when referring to the racemic mixture of two enantiomers. The suffix “Di-” is added to the compound number when referring to the equimolar mixture of two diastereomers. If only one of the two possible configurations at the boron center is considered, the stereo descriptor for the chiral boron center is included in the compound name.

Alongside the reported derivatization strategy, we have also investigated the combination of compound 56 with a transition metal center. More specifically, the connection of its donor moiety with a platinum center. Examples of compounds where boron-based chromophores are coupled with a
transition metal complex are not uncommon in literature, and they found application mainly in the fields of optoelectronics and chemical sensing. Boron-dipyrrromethenes (BODIPYs) are among the most frequently encountered fluorophores in this category of hybrid compounds due to their great fluorescence performances and photochemical stability. Nevertheless, other examples where the metal center is coupled to trisubstituted boranes or borylated phenyl pyridine moieties are also known. The group of Winter and co-workers published several studies involving molecules constituted by a platinum complex and a BODIPY chromophore. In the study of these mixed systems, they focused their attention on the influence of the heavy atom platinum on the photophysical and electrochemical properties of the boron-based dye and on the properties arising from the union of the two fragments.\textsuperscript{174, 194-199} The synthesis strategy they used to couple the metal center to the BODIPY scaffold is one of the simplest and elegant finds in the field of these hybrid emitters. It is based on the coupling between a platinum(0) complex and a bromoarene precursor via oxidative addition. We considered this reaction particularly appealing due to its simple implementation, high yield, and since we already intended to investigate the halogenation of our system, which would render the starting material for the reaction readily available.

3.2.1. Mono-halogenation

The mono-halogenation of the donor moiety was tested using compounds \textbf{36, 51} and \textbf{56}. By using NBS or NIS as the halogenating agents, we expected the functionalization to occur at the more electron-rich donor moiety, and we also expected the reaction to be highly regioselective. In accordance with the general mechanism of the electrophilic aromatic substitution reaction, we forecasted that the functionalization of the donor moiety would occur in para position with respect to the heteroatom since it should display the strongest directing effect.\textsuperscript{200-202}

Initial experiments showed that the donor moiety of compound \textbf{36} could be halogenated either using NBS or NIS. The bromination of compounds \textbf{51} and \textbf{56}, which share the same diphenyl sulfide donor moiety, delivered different results. Neither NBS nor bromine were effective in the bromination of \textbf{51} whereas, compound \textbf{56} could be brominated using NBS. These results show that the kind of donor cannot alone be used to forecast the outcome of this reaction and that other factors are playing a role in the halogenation of these compounds. Additionally, the iodination of compound \textbf{56}, using NIS, was tested. The reaction monitoring showed the complete conversion of \textit{N}-iodosuccinimide to succinimide but no significant conversion of \textbf{56} to another compound. Since the presence of moisture was ruled out, hydrolysis of NIS could be excluded, therefore additional investigations should be carried out to gather a better understanding of the reaction outcome. Further iodination experiments were not performed since an efficient bromination of \textbf{56} was already achieved and the investigation of the following derivatization steps was prioritized.

As already mentioned in the introduction to this chapter, we have concentrated our attention on the derivatization of compound \textbf{56}. Therefore, only the conditions for the bromination of \textbf{56} using NBS were optimized. Careful examination of the peaks obtained via \textit{1}H NMR spectroscopy confirmed that the halogenation displayed the expected regioselectivity (Fig. 47). A further confirmation of the molecular connectivity was provided by x-ray diffraction analysis which yielded the solid-state structure of compound \textit{En}-59. Isomers where the halogenation took place at different positions of the donor moieties could not be isolated. However, the reaction did not produce exclusively the above-mentioned compounds since other minor signals could be detected in the \textit{1}H NMR spectrum of the crude mixture.
By using equimolar amounts of 56 and NBS the reaction generated mainly the mono-halogenated compound En-59 but also about 10% of twofold brominated compound 60. As the concentration of 56 in the reaction mixture decreased, the bromination took place increasingly on the second phenylene ring of the donor of En-59. It was found that using a light deficiency of NBS, i.e., 0.9 eq., with respect to the starting material 56, delivers the most efficient conversion. Under these conditions, the amount of 60 generated was minimized, which ultimately simplified the chromatographic purification and did not generate a compound that was not of interest for the next steps. Moreover, unreacted 56 could readily be re-isolated and recycled in another bromination reaction.

After purification via column chromatography the amounts of the three isolated compounds added up to only 66% of the amount of starting material used. However, the traces of by-product generated in the reaction could not account alone for the low amount of isolated material, which suggest that the loss of material may be connected to the purification process. Analysis of the rather intense baseline spot observed in the TLC analysis by mass spectrometry delivered a value of 415 $m/z$ which could correspond to the mass of oxidized 56. Such an oxidation could take place at both the nitrogen atom of the quinoline moiety or at the sulfur atom of the donor unit. However, the oxidation of the heteroatoms in these fragments is normally performed with different oxidizing agents. Additionally, the lone pair of the nitrogen atom is already involved in the coordination with the boron center and it is therefore less likely to react. Performing the synthesis under inert conditions using dry and degassed solvents did not increase the yield of the desired product. Hashmat Ali et al. reported the oxidation of sulfides with NBS in the presence of hydrated silica gel, which would suggest that the oxidation could take place during the chromatographic separation. However, this process could be also ruled out, since the sub-stoichiometric amount of NBS was completely consumed at the end of the reaction, which could also be confirmed by NMR spectroscopy of the crude mixture.

The progress of the bromination reaction could be easily monitored via TLC. However, the amount of the components in the reaction mixture could be more precisely quantified via NMR spectroscopy.
Fig. 47: Spectrum 1: 1H NMR spectrum of 56; Spectrum 2: 1H NMR spectrum of En-59; Spectrum 3: 1H NMR spectrum of 60. Signals marked with \( \text{\textcopyright} \) are assigned to an unbrominated phenylene ring of the donor unit, signals marked with \( \text{\textcopyright} \) are assigned to a brominated phenylene ring of the donor unit. The solvent signal is marked with the symbol \( \text{\textregistered} \).

The comparison of the \( ^1\text{H} \) NMR spectra of the three isolated compounds 56, En-59 and 60 easily allows to identify those signals that can be assigned to the brominated phenylene ring of the donor unit (\( \text{\textcopyright} \); Fig. 47) and to the not brominated phenylene ring of the donor unit (\( \text{\textregistered} \), Fig. 47). The first bromination of the donor moiety clearly breaks the symmetry of this portion of the molecule, leading to seven \( ^1\text{H} \) NMR signals (Spectrum 2) instead of four (Spectrum 1). The unsubstituted phenylene ring has four protons and therefore yields 4 different signals in the \( ^1\text{H} \) NMR spectra. Specifically, two doublets for \( H_A \) and \( H_B \), and two pseudo-triplets for \( H_B \) and \( H_C \) (\( \text{\textcopyright} \), Fig. 47). Upon halogenation, \( H_B \) is substituted with a bromine atom and therefore for the brominated phenylene ring only three signals are observed (\( \text{\textregistered} \); Fig. 47). The bromine atom drastically reduces the coupling interaction between \( H_B \) and the two remaining hydrogen nuclei \( H_F \) and \( H_G \). The signal associated to \( H_E \) is therefore a sharp doublet with a small coupling constant of about 2.2 Hz which can be easily recognized. Protons \( H_F \) and \( H_G \) showed instead a doublet of doublet and a doublet multiplicity, respectively.

In compound En-59, the signals related to the non-brominated ring of the acceptor retain their multiplicity however the signal at 6.14 ppm is slightly shifted compared to the original signals of compound 56 found at 6.2 ppm. This small shift allows to distinguish and therefore separately quantify compounds 56 and En-59 in the crude mixture. In 60 only the set of signals typical of the brominated ring can be observed. The sharp signal at 6.25 ppm is slightly shifted with respect to the one observed in En-59, which is found at 6.29 ppm. This small difference again helped in the differentiation of the two compounds in the reaction crude. Monitoring and integrating the signals between 6.30 and 6.10 ppm was
therefore efficiently used to determine the ratios between the three species in the reaction mixture. The remaining signals can be assigned to the acceptor unit and are not significantly different in all three compounds.

3.2.2. Derivatization of compound En-59 and diastereomers separation

Having the racemic mixture En-59 at hand, we proceeded by investigating ways to introduce chiral auxiliaries to obtain separable diastereomers. As already mentioned, the choice of the auxiliary was also driven by its potential for further transformations after the separation of the two stereoisomers had been achieved.

We initially screened reactions involving some common chiral auxilaries (Fig. 48). The purpose of this was to gain insight into the general reactivity of the system and the separation of the obtained diastereomers. The installation of the residues was performed in the case of Di-61 and Di-62 via a palladium-catalyzed coupling reaction, whereas the coupling to the oxazolidinone residue of compound Di-63 was catalyzed with copper iodide. In all three cases, the NMR analysis of the purified material indicated that the desired product could be isolated, even though, in the case of compound Di-62, only in extremely small amounts. More precisely, the reaction delivered mainly de-halogenated compound 56. As expected, the ¹H NMR spectra of all three compounds displayed two sets of signals, one for each diastereomer. The most relevant results obtained with this first screening was that the separation of the two diastereomers of compound Di-61 could be achieved with standard flash chromatography techniques. This indicated that this kind of derivatization could indeed lead to a simple separation of the two stereoisomers if the right substituents were employed.

![Fig. 48 Derivatives of compound En-59 with three commonly used chiral auxiliaries. For each compound, two diastereomers are present due to the stereogenic spiro center.](image)

This first set of reactions delivered encouraging preliminary results concerning the derivatization of the precursor En-59. Compounds Di-62 an Di-63 displayed a similar luminescence to the brominated starting material. They are, therefore, two interesting examples of emitters with a chiral boron center. Conversely, compound Di-61 did not show any luminescence under standard atmospheric conditions, neither in solution nor in the solid-state. However, its two diastereomers could be separated, giving access to compounds where the chiral boron center was present exclusively in one of its two configurations.

To further develop this series of compounds, firstly, a reliable separation method for the diastereomer of compound Di-62 and Di-63 should be found. Only the isolation of the two different diastereomers would allow to analyze the influence that the chiral boron atom has on the photophysical properties of the emitters. Secondly, one or more derivatization or transformation procedures for compound Di-61 should be established to restore its luminescence and eventually provide a small library of derivatives.
In spite of the possibility offered by the three derivatives, our original aim was the synthesis of an even more varied set of compounds in which the chiral auxiliary should serve only as an instrument to achieve the separation of the stereoisomers and then allow their derivatization. We, therefore, decided not to investigate the derivatization of compound Di-61 or the separation of the diastereomer of Di-62 and Di-63. Instead, we tested the one-pot borylation procedures reported in Fig. 49. The aim of these reactions was the substitution of the bromide functionality with dialkoxo boryl substituents. This fragment would offer a more versatile tool for further transformations, and the employment of a chiral diol could still furnish two separable diastereomers. Both tested reactions consisted of a palladium-catalyzed borylation performed using either diisopropylamino borane or bis(pinacolato)diboron (B\textsubscript{2}pin\textsubscript{2}) as the boron source, followed by the transesterification of the borylated intermediate with a chiral diol.

![Fig. 49 Tested procedures for the palladium-catalyzed borylation of compound En-59 followed by transesterification with a chiral diol.](image)

The first reaction sequence (Fig. 49a), which was applied in a one-pot manner without isolating compound En-64, yielded the borinic acid ester Di-65 with a yield of 40% after purification via flash column chromatography. In the transesterification reaction, (+)pinanediol was used to replace the boron-bound pinacol. According to the results published by Brown and Roy, pinanediol forms a more stable ester than pinacol and can therefore displace the other diol.\textsuperscript{207} Attempts of isolating the pinacol intermediate En-64 via flash-column chromatography on silica gel unexpectedly resulted in a product yield of only 4%. This result suggests that compound En-64 may not be compatible with these purification conditions even though pinacol boronic acid esters are known to be highly stable compounds also when purified using standard column chromatography.
In the second reaction sequence (Fig. 49b), two more chiral diols could be tested, which would not be able to replace the pinacol in En-66. By quenching the coupling reaction with methanol, compound En-66 is converted to the boronic acid methyl ester, in which the methoxy groups can be more easily displaced. Mass spectrometry analysis together with $^1$H and $^{11}$B NMR spectroscopy confirmed the presence of the desired product in all the crude reaction mixtures. However, column chromatography failed in delivering pure samples of compound Di-67 and Di-68, which, most likely, also decomposed during the purification. Nonetheless, by following this procedure, compound Di-65 could be obtained with a yield of 46%. This second reaction protocol was then considered to be superior to the one previously illustrated not only because it displayed a slightly higher yield but mainly because the esterification process reached completion in less time and under much milder conditions.

Even though standard flash chromatography could be used to purify compound Di-65, this separation technique proved to be unsuitable for the separation of the two diastereomers. The two isomers were instead separated via semi-preparative HPLC using an Agilent Prep-Sil normal-phase column (21.2 mm X 250 mm), and the couple ethyl acetate-n-hexane as eluent. The separation was started using pure hexane and the ethyl acetate content was increased linearly up to 100% within 100 minutes. Two sharp bands associated with the two diastereomers were observed at 37.48 min and 38.36 min.

The $^1$H NMR spectra of the two separated diastereomers is reported in Fig. 50 and it is compared with the one of the diastereomers mixture. From the analysis of the peaks between 6.0 and 6.8 ppm it is possible to see how the signals in the mixture are constituted by two copies of the same signal each one slightly shifted with respect to the other. The sum of the peaks observed for the two separated diastereomers clearly yields the spectrum obtained for the mixture. The solution of the first eluted isomer which was prepared under standard atmospheric conditions and with not-dried CDCl$_3$ was analyzed again after a period of 7 days. The newly recorded spectrum showed no visible changes with respect to the first measurement. The fact that no signal of the second eluted isomer could be observed confirmed that the configuration of the stereocenter remains unaltered and does not undergo racemization at room temperature. The stability of the stereocenter is ensured by the strong coordination of the nitrogen atom.
to the boron center. Enantiopure derivatives obtained from one of the two isolated diastereomers should therefore be equally stable against racemization.

![Graph showing NMR spectra comparison](image)

**Fig. 50** Comparison between $^1$H NMR spectra (only aromatic region) of compound Di-65 (spectrum 1) and the spectra of the two isolated diastereomers. Spectrum 2: diastereomer with the boron atom in $S$ configuration. Spectrum 3: diastereomer with the boron atom in $R$ configuration. The solvent signal is marked with the symbol $\star$.

Crystals suitable for x-ray diffraction analysis were obtained from the first eluted fraction. Thanks to the obtained molecular structure it was possible to assign the stereochemical descriptors to the boron center and subsequently derive the one of the second isomer. As depicted in Fig. 51, the chiral center in correspondence of the boron atom of the crystalized diastereomer has an (S) configuration. This assignment implies that the (R) configurator can be assigned to the spiro-boron center of the second eluted diastereomer.

![Ortep drawing of solid-state structure](image)

**Fig. 51** ORTEP drawing of the solid-state structure of $S$-65, hydrogen atoms are omitted for clarity.

Both isolated diastereomers were analyzed using circular dichroism spectroscopy as a first evaluation for the effect produced by the introduction of a chiral center in correspondence to the boron atom (see chapter 3.4.3)
3.2.3. Derivatization of compound Di-65 via Suzuki-Miyaura coupling

In this chapter, some explorative studies on the derivatization of compound Di-65 are presented. The final aim of these next experiments was to find a suitable procedure to substitute the pinane dioxyboryl moiety of the isolated diastereomers with a non-chiral substituent to obtain a couple of pure enantiomers. Boronic acids and boronic acid esters are highly versatile building blocks and can undergo a wide range of reactions. As a first proof of concept, we decided to test Di-65 in the well-known and widely applied Suzuki-Miyaura coupling. We opted for this reaction since many different conditions had been reported in the literature and would have allowed us to easily adjust them to our substrate. Moreover, by simply changing the halogenated reaction partner, many different derivatives could be potentially prepared.

The coupling reaction was performed using a modified version of procedure reported by Zhou et al., which had been successfully applied in our research group in other occasions. These conditions are particularly mild, and the reaction normally reached completion in about 1 h. The detailed reaction conditions are summarized in Fig. 52 whereas the substrates used in the screening are reported in Table 1. The brominated substrates that had been tested included benzene derivatives with different substituents, 2-bromothiophene and 4-bromopyridine.

![Reaction condition for the Suzuki-Miyaura coupling between Di-65 and different brominated precursors.](image)

*Fig. 52 Reaction condition for the Suzuki-Miyaura coupling between Di-65 and different brominated precursors.*
The reaction towards compounds En-70, En-71 and En-72 indeed reached completion in 1 or 2 h; however, for compound En-69, where an electron-donating substituent was installed, the reaction time had to be considerably extended.

We discovered that the presence of PPh₃ (entry 1-3) led to the formation of En-73 as a by-product (Fig. 53). This was confirmed by mass and NMR spectroscopy and could be attributed to the transfer of a phenyl substituent from the phosphine ligand. In the coupling of entry 1, characterized by a slower reaction rate, the TLC analysis of the crude material revealed the formation of a considerable amount of the by-product which was visually estimated to be at least equal to the amount of desired product. The relative distribution of the two products was not determined but this observation showed that this side reaction was highly competing with the slower Suzuki-Miyaura coupling. The strong similarity of En-73 with the target molecules greatly complicated the purification via column chromatography of the reaction mixtures. In the case of entry 2, the high similarity in retention times between compounds En-70 and En-73 rendered it impossible to obtain pure En-70 using standard chromatographic techniques. This transfer process had been previously reported in the literature, and high catalyst or ligand loadings are known factors that promote this side-reaction. ²⁰⁹, ²¹⁰

<table>
<thead>
<tr>
<th>Entry</th>
<th>R-Br</th>
<th>Product</th>
<th>PR₃</th>
<th>Reaction time</th>
<th>By-product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>En-69</td>
<td>PPh₃</td>
<td>16 h</td>
<td>En-73</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>En-70</td>
<td>PPh₃</td>
<td>1 h</td>
<td>En-73</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>En-71</td>
<td>PPh₃</td>
<td>1 h</td>
<td>En-73</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>En-71</td>
<td>P(o-tolyl)₃</td>
<td>1 h</td>
<td>En-74</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>En-72</td>
<td>P(o-tolyl)₃</td>
<td>2 h</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 1 Summary of the phosphine and substrate screening for the Suzuki-Miyaura coupling between Di-65 and different brominated precursors.
Indeed, in all the reactions reported in Table 1, these two species’ concentration was relatively high, with 40 mol% and 20 mol% for the ligand and the catalyst, respectively. In some reported cases, the use of tris(o-tolyl)- or trimesityl-phosphines proved to be effective in suppressing the transfer reaction. Thanks to the higher steric hindrance of the substituents, the formation of a metalacyclic intermediate responsible for the transfer reaction should be disfavoured. For this reason, in entries 4 and 5, tris(o-tolyl)-phosphine was employed as the ligand. However, in both entries, the formation of the transfer-by-product En-74 could still be observed. Surprisingly, in entry 6, were 2-bromopyridine was used as brominated substrate, a different by-product was generated. Analysis via mass spectrometry and NMR spectroscopy suggested that the molecule corresponded to compound 75 (Fig. 53). This species could be generated by the homocoupling reaction between two molecules of Di-65. As reported by Adamo et al., this homo-coupling reaction can be promoted by the presence of oxygen since it proceeds via the formation of a palladium-peroxo complex. However, the experiment of entry 6 as well as all the other present in this chapter were conducted parallel under inert atmosphere and using the same degassed solvents. The same reaction was additionally repeated to exclude that air accidentally leaked into the reaction vessel, but the experiment delivered the same outcome. Further investigations are therefore needed to better understand which factor could be responsible for the formation of this by-product. The performed reactions were undoubtedly affected by the high catalyst and ligand loading. Further tests need to be performed to quantify in which extent the reduction of the ligand and catalyst loading would limit the generation of by-products.

With the reported coupling protocol, it was possible to obtain small amounts of pure derivatized compounds En-69 and En-71 in 9% and 32% yield, respectively. However, for compound En-70 and En-72 the tested purification conditions did not yield the product in a pure form. A small separation test using HPLC with chiral stationary phase was also performed to evaluate whether the separation of the two enantiomers could be also performed after the coupling reaction. The separations of compounds En-71 and En-69 were tested using either DCM-Hexane or isopropanol-hexane as the eluting mixture and either a chiralpack® 1A (250 × 4.6 mm, 5 μm) or an (S,S) Whelk-OBE®-1 (250 × 4.6 mm, 5 μm) column. Unfortunately, under these conditions no separation was observed. Even though a wide variety of chiral stationary phases is nowadays available, and a wide variety of eluents could still be tested we believed that the separation of the two diastereomers of Di-65 remains a more convenient procedure. The separation could be more easily upscaled and makes use of a considerably cheaper stationary phase.

In entry 5 (Table 1) we specifically aimed for the introduction of a nitrogen-containing substituent for a particular reason. We expected, that such a moiety would provide a handy tool to confirm retention of the boron stereo center configuration after the coupling reaction. The protonation of the nitrogen atom

![Fig. 53 By-products detected in the Suzuki-Miyaura coupling between Di-65 and different brominated precursors (Table 1).]
with a chiral acid would lead to the production of a diastereomeric salt. Therefore, after the protonation, two different diastereomers should be detected if racemization of the chiral boron center of a pure enantiomer occurred. According to our findings discussed before (Fig. 50), we expected that the presence of a pair of diastereomers could be easily confirmed via NMR spectroscopy. The comparison between the two $^1H$ NMR spectra reported in Fig. 54 show the effect produced by the protonation of En-72 with (1S)-10-camphorsulfonic acid. The reaction between the racemic mixture and the chiral acid caused the shift of the recorded signal and induced a splitting of the signals into two symmetric sets. The outcome of this experiment confirmed the validity of our hypothesis and of the utility of the pyridyl substituent as a probe for the configurational changes of the stereocenter at the boron atom.

![Fig. 54](image)

**Fig. 54** Influence of the interaction between compound En-72 and a chiral acid on the aromatic region of the $^1H$ NMR. Before (spectrum 1) and after (spectrum 2) the addition of (1S)-10-camphorsulfonic acid. The generation of two sets of signals in a 1:1 ratio confirms the production of two diastereomeric salts.

Due to the limited availability of the separated diastereomers, the above-mentioned reaction was performed only with the racemic mixture En-72. It is also worth noting that enantiomers resolution through diastereomeric salt formation is a commonly employed method. It is therefore possible that the two diastereomers produced by the addition of the chiral acid may be possibly separated via crystallization.

### 3.2.4. Introduction of a transition metal center

Having compound En-59 at hand also allowed us to investigate the connection of a transition-metal center to the donor fragment of this chromophore. More specifically, using compound En-59 as the brominated precursor, we applied the metalation protocol developed by Winter and co-workers reported
in Fig. 55. This procedure allows the introduction of a platinum center under mild conditions by means of an oxidative addition reaction between a suitable halogenated precursor and Pt(η^2-C_2H_4)(PEt_3)_2. The Pt^0 complex is generated in situ by thermal treatment of Pt^II(Et)_2(PEt_3)_2. The thermally promoted reaction proceeds via β-hydride elimination followed by reductive elimination of ethane. The only by-products generated by the reactions are therefore ethane, and ethene, which acts as a labile ligand attached to the Pt^0. The experiment was conducted using the racemic mixture of En-59. To obtain the product in an enantiomeric pure form, the metalation procedure must be modified so that the accessible diastereomeric compounds R-65 or S-65 could be used as starting material. Alternatively, the isolated enantiomers of the brominated precursor could be possibly generated by the halogenation of the separated diastereomers of Di-65.

The complex Pt(η^2-C_2H_4)(PEt_3)_2 was generated by simple thermal treatment of Pt(Et)_2(PEt_3)_2 in benzene at 110 °C. After the analysis via ^1H and ^31P NMR spectroscopy confirmed the completion of the reaction, En-59 was added and the conversion of the brominated species was monitored with the same spectroscopic techniques.

Upon addition of En-59 at room temperature, different sets of signals could be detected in the ^31P NMR. However, these peaks could not be clearly assigned to specific species. As already highlighted in the works of Winter and co-workers as well as of van der Boom and co-workers, this reaction can generate other than the two expected oxidative addition products En-76-trans and its cis isomer, also the η^2 complexes where the ethylene ligand is replaced by a double bond of the brominated starting material. Both working groups have additionally showed that thermal treatment of the reaction mixture converted completely the η^2 complexes to the oxidative addition products. Also in our case, heating the reaction mixture led to a change of the product distribution and to a simplification of the NMR spectra. After treating the solution first at 50 °C for 1 h and then at 70 °C for 4 h, the ^31P NMR spectrum displayed what looked like one signal with a doublet multiplicity and with two satellites at 12.32 ppm. The number of signal and the observed multiplicity were not in agreement with neither of the two expected reaction products namely En-76-trans and its cis isomers. However, crystals suitable for X-rays diffraction analysis were obtained from the reaction mixture. Analysis of these crystals yielded the molecular structure reported Fig. 56, corresponding to compound En-76-trans. The signal observed in the ^31P NMR spectrum could then be explained with the combination of two doublets, with a frequency difference close to the coupling constant between the two phosphorous nuclei.
This hypothesis was further confirmed by the comparison of the obtained spectrum with the simulated spectrum calculated with Spinworks4 and by measuring the same spectra with two different spectrometers, equipped with magnets characterized by different magnetic strengths.

Since the $^1$H NMR spectrum of the crude material showed some traces of the brominated starting material En-59, the mixture was subjected to purification via flash column chromatography. The chromatographic separation indeed removed the unwanted brominated compound, however, in the $^{31}$P NMR spectrum a small new signal could be observed. This outcome indicated that either different conditions for the chromatographic separation must be tested or a different method must be employed (e.g. crystallization) for the purification of this compound. Unfortunately, the optimization of the purification procedure as well as an in-depth characterization of this compound could not be performed in the context of this work. However, we could successfully show that the chiral brominated compound En-59 could be also coupled to a Pt complex fragment. This modification could have an impact on the optical behavior of the TADF emitter and therefore open new possibilities regarding its potential applications. For instance, connection between TADF emitters and a platinum complex fragment had been recently used to obtain novel anti-cancer phototherapy agents and platinum-based chromophores with a remarkably short, excited state lifetime.$^{217, 218}$
3.3. Solid-state structures

Of all the compounds for which the syntheses are described in chapter 3.1 and for the derivatives Di-65, En-69, En-76-trans and 77 (Fig. 58), it was possible to obtain crystals suitable for x-ray diffraction analysis and consequently their solid-state structure. The reason that brought us to include compound 77 in this thesis and its generation are are illustrated later in chapter 5.2.2.2. The values of the structural parameters discussed in this chapter for every compound are reported in Table 2 and Table 3 (chapter 3.3.5). Every compound has different packing modes which, however, display two common features. The acceptor moieties are disposed on parallel planes and a C-H/π hydrogen bond interaction between one C-H bond of the acceptor moiety and an aromatic ring of the donor is always observed.

Fig. 58 Molecular structure of compound 77. This compound is object of chapter 5.2.2.2.

3.3.1. Donor fragment

The major difference between the solid-state structures of the compounds obtained in this work and the related compound 47, previously reported by Ingleson and co-workers, is evident when the side-views of the two structures are compared (Fig. 59). Compound 55 will be taken as element of comparison but the consideration that will be made are valid for all the compounds analyzed. In the structure of compound 47 the biphenyl unit is planar, with its best plane slightly bending towards the nitrogen atom of the phenylpyridine fragment. The donor and the acceptor are almost orthogonal with respect to each other, displaying an angle between the two best planes of 85.57(6)°. The donor moiety of 55 is also bent towards the nitrogen atom of the acceptor unit but it is additionally folded along the B-S vector (Fig. 60). Due to this structural difference the three ring systems of the acceptor moiety are not coplanar as in compound 47 and the atoms of the central ring do not lay on the same plane.

Fig. 59 Side views of the solid state structures of compounds 47 and 55.
In all the obtained solid-state structures, the donor moiety is folded along the B-S or B-N vector with different degrees of magnitude. This structural feature was quantified by defining a donor’s folding angle, which was obtained by measuring the angle between the best planes of the two outer aromatic rings of the donor unit (Fig. 60). The values range from 1.07(15)° for En-76-trans to 40.73(6)° for 55 (Table 2). No direct correlation between the folding angle and any other parameter could be found.

![Side views of the solid state structure of compound 55 and the same structure viewed from the B-S vector. The best planes passing from the outer aromatic rings of the donor moiety are highlighted as well as the angle between them to which is referred as donor’s folding angle in this work.](image)

Fig. 60 Side views of the solid state structure of compound 55 and the same structure viewed from the B-S vector. The best planes passing from the outer aromatic rings of the donor moiety are highlighted as well as the angle between them to which is referred as donor’s folding angle in this work.

An analogous structural behavior was reported in the works of Yorimitsu and coworkers and in the work of Rault-Berthelot and Poriel et al. In these publications the thioxanthene fragment of the reported molecules was also folded whereas a biphenyl fragment introduced at the same position was planar.\textsuperscript{219-221} Rault-Berthelot and Poriel additionally showed that double oxidation of the sulfur atom introduces more rigidity in the moiety, therefore, diminishing the folding angle. In our case, mono-oxidation of the sulfur atom of 55 only had a negligible influence. The folding angle of the two compounds changed from 40.73(6)° (compound 55) to 40.52(5)° (compound 77) upon oxidation of the sulfur atom.

The major implication of a bent donor moiety is that two different conformations for every molecule are theoretically possible. One conformation presents the nitrogen atom of the acceptor unit at the concave side of the folded donor, whereas the other conformation has the nitrogen at the convex side (Fig. 61).
Indeed, the solid-state structures of compounds 47, 50 and 52 showed positional disorder and contained both conformations in different ratios. In the NMR spectra of these compounds, only one set of signals for the donor moiety could be observed for each compound, suggesting a fast interconversion between the two conformers. We also have excluded that the conversion between the two conformers proceeds through the cleavage of one of the carbon-boron bonds. This mechanism would generate an intermediate with a tricoordinated boron atom, prone to hydrolysis under atmospheric conditions. The stability which was not observed for any of the obtained compounds.

3.3.2. Acceptor fragment

In the case of the otherwise symmetric phenylpyridine and benzo[h]quinoline unit, a correct assignment of the boron-bonded nitrogen and carbon atoms is crucial for the distinction between the two different conformers mentioned in the previous chapter. Such assignment is not trivial due to the small difference between the two elements’ atomic numbers. A confirmation of a correct assignment was obtained by interchanging the two atoms and comparing the obtained $R$ values and the equivalent isotropic displacement parameter $U_{eq}$ for the two atoms. In the case of 51, interchanging the two atoms delivered the two different $R$ values of 2.75% and 3.56% and the two different couples of equivalent isotropic displacement parameters ($U_{eq}(C1)/U_{eq}(N1) 0.018/0.019$ and $0.013/0.025$). The structure with the lower $R$ factor and the balanced ratio between the equivalent isotropic displacement parameter was then considered as the correct solution.

The boron-carbon and boron-nitrogen bond lengths are comparable with the one observed in the previously reported compounds 26 and 47. All acceptor moieties are planar with a maximum deviation of 0.2119(11) Å from the best plane (compound 57). The compounds that display a major deviation from planarity are those equipped with either a 2-phenylquinoline or a 2-phenylbenzo[g]quinoline acceptor fragment.

Due to the constraints exerted from the phenyl pyridine fragment, the measured N-B-C angles at the acceptor (denoted also as bite angles, Fig. 62) are lower than the theoretical value expected for a tetracoordinated atom. The measured values for the bite angles range from 94.1(8)° (for compound 50) to 99.3(1)° (for compound 54). As a result of the coordination to the boron, the acceptor fragment bends towards the boron center. In the benzo[h]quinoline-based acceptor this effect is less pronounced since
the fragment itself is less flexible and as a consequence, the B-N bonds are longer with lengths of 1.6813(17) Å and 1.604(18) Å for \( 53 \) and \( 54 \), respectively. The different degree of flexibility of the donor can also be quantified by measuring the angle between the C3-C6 and C7-C10 vector (denoted as kink angle, Fig. 62). The kink angle for compounds \( 53 \) and \( 54 \) is 9.67(4)° and 16.1(2)°, respectively, which confirms the higher degree of rigidity of the benzo[h]quinoline fragment.

![Side views of the ORTEPs of compounds 53 and 54 highlighting different donor rigidities and the acceptor bite angles.](image)

Fig. 62 Side views of the ORTEPs of compounds 53 and 54 highlighting different donor rigidities and the acceptor bite angles.

### 3.3.3. Compound En-76-trans

In the solid-state structure of compound \textit{En-76-trans}, the portion of the original chromophore displays positional disorder, and two different structures can be observed. The two molecules differ mainly for the extent with which the donor fragment folds while they share the same structural parameters regarding the platinum center. In one of the structures, the donor is moderately folded displaying a folding angle of 25.62(38)° (Fig. 56). In the second molecule instead, the donor is nearly planar and has a folding angle of only 1.07(15)° (Fig. 64). In both structures the acceptor moiety retains the same orientation although being slightly shifted.

The structural parameters associated with the platinum center in compound \textit{En-76-trans} were compared to the one of the two BODIPY platinum complexes \( 78 \) and \( 79 \) reported by Winter and co-workers.\(^{174}\) The two complexes represented an interesting term of comparison due to their peculiar photophysical properties. In these examples, the combination of the platinum complex fragment and the boron-based dye yielded two chromophores which displayed a double emission and showed both fluorescence and phosphorescence. As an additional term of comparison also the trans-Pt(aryl)(PEt\(_3\))\(_2\)Br complexes \( 80, 81 \) and \( 82 \) were considered (Fig. 63).\(^{222-224}\) The parameters discussed in this chapter are reported in Table 3, together with the values measured for the above-mentioned compounds.
As expected from a square planar coordination geometry, in **En-76-trans** the ligands of the platinum lay on one plane and the sum of the angles between them adds up to 360°. The Br-Pt-P angles are, however, between 0.14 and 3.03° lower than the C-Pt-P angles. This light difference would suggest the presence of a weak repulsive interaction between the phosphine ligands and the donor-spiro-acceptor backbone. This behavior had been observed in all the complexes used as comparison made exception for compound **82** which also has the least sterically demanding σ-aryl ligand between all the considered compounds. In **En-76-trans**, the coordination plane is tilted with respect to the best plane passing through the connected aromatic ring of 87.52(12)° or 71.96(80)° (Fig. 64), which is in accordance with the values obtained for the reference compounds.

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**Fig. 63** Platinum complex used as element of comparison in the analysis of the solid-state structure of compound **En-76-trans**.

**Fig. 64** ORTEPs of one of the two molecules observed in the solid-state structure of compound **En-76-trans**. The coordination plane is highlighted in green whereas the best plane passing through the coordinated aromatic ring is highlighted in blue.
In complex En-76-trans, the lengths of the bonds between the platinum center and its ligands are in line with the one reported in the literature. As reported by Winter and co-workers, the length of the Pt-C bond in particular, plays an important role in the magnitude with which the platinum center influences the photophysical properties of the emitter.\textsuperscript{174} In platinum BODIPY complexes, shortening the Pt-C distance enhances the intersystem crossing (ISC) efficiency thereby promoting the emission via phosphorescence from a ligand-centered tripled excited state. Compound 78 showed, in fact, a higher phosphorescence quantum yield than 79 due to the shorter Pt-C bonding distance. The Pt-C bond length of compound En-76-trans lies within the range defined by the values observed for 80, 81 and 82. The observed value is, however, closer to the one measured for compound 79 than for 78. This observation may suggest that the influence of the platinum complex fragment would produce only a moderate effect on the photophysical properties of the complex. Nevertheless, as mentioned by the same authors, many interplaying factors determine the photophysical properties of an emitter and the bond length alone cannot be used to provide a reliable prediction.

3.3.4. Conclusion

In summary, the solid-state structure of the compounds synthesized in this work differentiate from the one of compound 47 mainly for the lower rigidity exhibited by the donor moiety which can fold along the B-S or B-N vector. This structural feature allows the existence of two different conformations, one with the heteroatom of the acceptor fragment positions at the concave side of the donor and one with the heteroatom at the convex side. The analysis of the solid-state structures showed also that a difference in flexibility can be observed between the different acceptor moieties. The benzo[h]quinoline moiety is the acceptor fragment with the highest rigidity which is also reflected by the higher length of the bond between the acceptor and the boron center. The structural parameter of the platinum center in En-76-trans are comparable to the one of the chosen reference examples. In the specific case of compounds 78 and 79, the Pt-C bond had proved to be a crucial parameter in determining the extent with which the platinum center influenced the emission of the chromophores. The analysis of the photophysical properties of En-76-trans and other derivatives is therefore of interest to evaluate whether a similar effect is observed for this class of chromophores.
### 3.3.5. Tables

#### 3.3.5.1. General structure parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B-C(^a)</td>
<td>B-N</td>
</tr>
<tr>
<td>27</td>
<td>1.620(5)</td>
<td>1.626(5)</td>
</tr>
<tr>
<td>47</td>
<td>1.610(4)</td>
<td>1.617(5)</td>
</tr>
<tr>
<td>36</td>
<td>1.602(4)</td>
<td>1.637(4)</td>
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<td>50</td>
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<tr>
<td></td>
<td>Molecule 2</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</table>

*Table 2 Selected bond lengths and angles used in the comparison between the solid-state structure of the investigated chromophores. a) length of the bond between the boron atom and the carbon of the acceptor moiety, b) length of the bond between the boron atom and the two carbon atoms at the acceptor moiety, c) length of the central C-C bond at the acceptor fragment, between C6 and C7 (Fig. 62).*
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond length (Å)</th>
<th>Angle (°)</th>
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</thead>
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<td>Pt—P</td>
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</tr>
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</table>

Table 2 Continues from the previous page.

### 3.3.5.2. Structural parameters related to the platinum center

Table 3 Specific bond lengths and angles used in the comparison between the platinum center of En-76-trans and the one of other related platinum complexes. a) angle between the coordination plane and the best plane passing from the ring system attached to the platinum atom.
3.4. Photophysical properties

The photophysical properties of the newly synthesized donor-spiro-acceptor compounds were analyzed by means of absorption and fluorescence spectroscopy, and the excited-state lifetimes of the fluorophores were measured via time-correlated single-photon counting (TCSPC) measurements. As illustrated in the introduction of this thesis, such analysis was fundamental to confirm the forecasted formation of a charge-transfer excited state, the involvement of a triplet excited states in the radiative processes, and ultimately confirm the emission via TADF.

The measurements were conducted using both solutions of the emitters and thin-layer polymeric films doped with 5 wt% of the fluorophores. To provide additional elements of comparison, some of the photophysical properties of compounds 83 (Fig. 65) are also reported.

![Fig. 65 Molecular structure of compound 83.](image)

3.4.1. Measurements in solution

The reported analyses were performed using toluene as the solvent unless otherwise specified. A summary of the most relevant photophysical data is reported in Table 4 at the end of the chapter.

3.4.1.1. Absorption spectra

For all the analyzed emitters, the lower-energy region of the absorption spectra is strongly dominated by the absorption of the acceptor moiety. It follows that the absorption onset of compounds that share the same acceptor fragment does not change significantly. For instance, in the case of compounds 53, 55, and 83, the portion of the absorption spectra at low energies is almost identical even though the first two compounds are equipped with two different donor moieties and the last with no donor fragment at all. The change of donor affects the absorption spectra but only at lower wavelengths (Fig. 66a, b). A noticeable difference in the absorption onset was instead observed when compounds equipped with different acceptors are compared, as in the case of compounds 51, 56 and 57 (Fig. 66c). Specifically, the onset shifts to a higher wavelength the more aromatic rings are annulated to the pyridyl ring of the acceptor. Compounds 55 and 56 have both three aromatic rings at the acceptor, but with a radically different annulation pattern; nonetheless, the two compounds showed a nearly identical absorption onset.

In line with the above-mentioned observations, the donor moiety’s functionalization did not induce a radical change in the absorption onset. The bromination in compound En-59 hardly caused any changes in the absorption spectra compared to the one of the parent compound 56. The introduction of the
pinanediol boryl ester residue in Di-65 or the two differently substituted phenyl derivatives in En-69 and En-71 led to the detection of an additional band at 306 nm, 309 nm, and 324 nm, respectively (Fig. 66b).

The strong similarity between the initial part of the emitters absorption spectra and the spectra of the separated acceptor fragments, together with the relatively high molar extinction coefficients (ranging from 0.4819 L cm⁻¹ mol⁻¹ to 2.318 L cm⁻¹ mol⁻¹), drove us to suppose that the observed transition is related to the formation of a locally-excited state centered on the acceptor fragments (most likely involving a ππ* transition). This scenario would be in agreement with what had been observed for the emitters reported by Wu, Chou, Chi, and co-workers (chapter 1.3.2.1). Unlike some other TADF emitters, no weak absorption band associated with the direct excitation of the CT excited state was observed. The bands of these transitions are normally red-shifted with respect to the one associated with the excitation of the locally-excited state. They are also much weaker due to the lower oscillator strength associated with the transition. Even the weak band around 450 nm recorded for compound 57 cannot be attributed to the excitation to the charge-transfer excited state since it can also be observed in the absorption spectra of the borylated precursor 45.

![Absorption spectra comparison](https://example.com/spectra.png)

*Fig. 66 Comparison of the absorption spectra of different compounds in toluene solution a) emitters with identical acceptor moiety but different or no donor fragment, b) emitters with same acceptor moiety but different donor, c) emitters with different acceptor moiety but the same donor.*
3.4.1.2. Fluorescence spectroscopy

3.4.1.2.1. Fluorescence emission

All the examined compounds show a broad and structureless emission characterized by a large Stokes shift ranging from 9,123 to 18,298 cm\(^{-1}\). These two characteristics are a strong indication that the observed emissions take place from a charge-transfer excited state. This hypothesis was then further confirmed by analyzing the influence of the solvent polarity on the emission spectra (chapter 3.4.1.2.2). In comparison, the emission detected for compound 83, where the donor fragment is not present, is significantly different. The emission peak is characterized by a relatively small Stokes shift (1140 cm\(^{-1}\)), and its structure resembles the low-wavelength region of the absorption spectra (Fig. 67a). A broad emission peak with a more significant Stokes shift was observed if the emitter was excited at higher energies, far from its absorption onset. However, the origin and nature of the second emission band were not investigated. Nonetheless, comparing the emission of compound 83 with the emission profiles of the other donor-acceptor emitters validated the hypothesis that a charge-transfer excited state is responsible for the emission.

The emission spectra measured under aerated and degassed conditions were nearly identical. Removing the air from the sample, however, caused an increase in the emission intensity. Since under the two conditions, the energies associated with the emission peaks remained unchanged, we concluded that in both cases, the emission took place from the same excited state and that no additional phosphorescence emission was observed.

![Fig. 67 a) Absorption and emission spectra of compound 83. The emission spectra were obtained by exciting the sample at either 300 nm or 360 nm. b) Absorption and emission spectra of compounds 53 and 55. The emission spectra were obtained by exciting the samples at 375 nm. The comparison highlights how the donor-acceptor architecture in compounds 53 and 55 promotes the emission from a charge-transfer excited state](image)

3.4.1.2.1.1. Emission wavelength and the strength of the donor and acceptor fragments

As previously mentioned, we expected that modifying the donor and acceptor fragment would introduce an alteration of the HOMO and LUMO energies, thereby inducing a change in the energy associated with the fluorescent emission. This assumption proved to be valid since the fluorescence emissions varied depending on the relative strength of the donor and acceptor fragments. Specifically, it could be observed that an increase of the donor and/or acceptor strength translated into an increase in the emission wavelength and the other way around. The observed trend is also in agreement with the
calculation reported in our published work and the data obtained from the cyclic voltammetry measurements (chapter 3.5).\textsuperscript{226}

Thanks to the combination of different donor and acceptor fragments, the fluorescence emission of the synthesized compounds covered a relatively wide range of the visible spectrum. The two extremes of the interval were represented by compound \textbf{51}, which displayed an emission maximum at 526 nm, and compound \textbf{57} with an emission maximum at 683 nm. The effect of the donor strength on the fluorescence emission is exemplified by the comparison between the emission spectra of compounds \textbf{36}, \textbf{50} and \textbf{51} (Fig. 68a, blue lines). These compounds share the same phenylpyridine-based acceptor moiety but have different donor fragments, which are characterized by an increasing electron-donating ability following the order \textbf{51}, \textbf{36}, \textbf{50}. As the strength of the donor increases, a marked red-shift of the fluorescence emission is observed as a higher donor strength destabilizes the HOMO, thus reducing the HOMO-LUMO gap. This general behavior was observed for all the examined compounds, independently from the acceptor unit (i.e., the emitters with a benzo[h]quinoline-based acceptor Fig. 68a, green lines). It could also be observed that, in terms of energy, the exchange between two different donor moieties generates a similar shift of the observed emission, independently from the acceptor moiety installed in the molecular scaffold. For instance, exchanging the diphenyl sulfide-based donor with the diphenyl methylamine-based donor produces a bathochromic shift of the emission of \(2,87 \times 10^{-1}\) eV, \(3,11 \times 10^{-1}\) eV and \(3,02 \times 10^{-1}\) eV for the compounds with a phenylpyridine, 2-phenylquinoline and benzo[h]quinoline acceptor, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure68.png}
\caption{a) Influence of the donor strength on the emission spectra of compounds with a phenylpyridine-based acceptor moiety and a benzo[h]quinoline acceptor moiety. Spectra with the same are from molecules that share the same acceptor, lines with the same style share the same donor. b) Influence of the acceptor strength on the emission spectra of compounds with diphenylsulfide-based donor moiety.}
\end{figure}

The effect of the acceptor strength on the emission wavelength can be similarly discussed and can be exemplified by the comparison between the fluorescent emission of compounds \textbf{51}, \textbf{56} and \textbf{57} (Fig. 68b). These three emitters possess an increased number of annulated aromatic rings at the acceptor pyridyl ring. The extension of the conjugated system increasingly stabilizes the acceptor’s \(\pi^*\) orbital leading to an increase of the accepting strength of the fragment and, therefore, to a decrease of the HOMO-LUMO energy difference. This observation also indicates a substantial contribution of the \(\pi^*\) orbitals of the acceptor unit to the LUMO of the emitter.
In contrast with what can be observed for their absorption spectra, compound 55 and 56 displayed a noticeable difference in their fluorescence emission. In particular, the emission maxima of compound 55 is blue-shifted by 47 nm (0.17 eV) compared to the one of compound 56. This observation suggests that the LUMO localized on the 2-phenyl quinoline acceptor has a slightly lower energy compared to the one based on the benzo[h]quinoline moiety.

Fluorination of the acceptor does not have a marked influence on the emission spectra. The difference between the emission maxima of compounds 36 and 52 is only 5 nm (1.71·10⁻² eV). This observation is in line with the one reported by Wu, Chou, Chi, and co-worker for the related emitters.¹⁰³ However, as reported in the next chapter, a difference between these two compounds can be observed when the excited state lifetime is analyzed. Derivatization of the donor moiety influences the emission wavelength more than the fluorination of the acceptor but in a minor way compared to the complete exchange of the donor fragment itself. Introduction of electronegative substituents as bromine in compound En-59 or 4-(trifluoromethyl)phenyl in compound En-71 lead to a hypsochromic shift of the emission, which is connected to a slight reduction of the donor strength. The same effect is observed for compound Di-65, where the boron atom with its intrinsic electron-deficient nature induces the same effect. A slight bathochromic shift is instead observed for compound En-69, where the electron-donating substituent 4-methoxyphenyl slightly increases the strength of the donor.

3.4.1.2.2. Solvatochromism

Analyzing the influence of solvent polarity on the absorption and emission spectra delivers information about the nature of the excited states. In this work, it was used as a method to confirm that the fluorescence emission of the chromophores took place from a charge-transfer excited state (CT). In the specific case of compound 56, the absorption spectra underwent minimal changes when solvents with different polarities were used in the measurement. The lowest value for the absorption onset was registered for the acetonitrile solution at 382 nm and the highest value for the toluene solution at 391 nm, which correspond to an energy difference of 74.7 meV. In contrast, the solvent employed in the measurement had a much more significant influence on the emission spectra of the same chromophores. Specifically, when a solvent with greater polarity was used, a bathochromic shift of the emission maximum was observed and vice versa (Fig. 69). The lowest and highest value of the emission maxima were recorded for the hexane (575 nm) and acetonitrile (675 nm) solutions, respectively, accounting for an energy difference of 319.4 meV.

The observation of positive solvatochromism further confirmed that the excited state responsible for the emission has a charge-transfer character. The highly polarized charge-transfer excited states can establish strong interactions with polar solvents, leading to the stabilization of the excited molecule. Conversely, apolar solvents as n-hexane cannot provide the same interactions and the related stabilizing effect. This difference is what ultimately causes a decrease of the charge-transfer excited state energy with the increase of the solvent polarity and the consequent red-shift of the emission.
3.4.1.2.3. **Excited-state lifetimes**

The participation of triplet excited states in the radiative decay process is at the basis of TADF. Being tripled excited states strongly quenched by oxygen, comparing the measurement of the excited state lifetime performed in the presence or absence of air is a standard experiment used to confirm the involvement of such excited states in the radiative processes. To remove oxygen from the samples measured in this work, the solutions were subjected to four freeze-pump-thaw cycles in a cuvette equipped with a Teflon valve and the cuvettes were then left under vacuum during the whole measurement. The available pulsed sources for the TCSPC measurements were a flashlamp (with a maximum pulse frequency of 300 Hz), three different lasers with emission at 405 nm, 450 nm, and 485 nm, together with a photodiode emitting at 320 nm. For all the TCSPC measurements, we decided to employ the photodiode since its emission wavelength was reasonably close to the absorption onset of the compound with a phenylpyridine-based acceptor. The same was not true for the emitters with other acceptor units, but the excitation energy provided by all the laser sources was too low to excite the chromophores, whereas the duration of the flashlamp pulse was longer than the excited state lifetimes of most chromophores. Three exceptions were represented by compounds 57, 55 and En-59. The laser emitting at 405 nm could be used to excite compound 57 due to its extended absorption. Whereas for the last two fluorophores also the xenon flash lamp had to be employed due to the extraordinary long excited state lifetime displayed by the chromophores.

As reported in Table 4, for compounds 50, 53 and 54 only one decay regime was observed, and the exclusion of air led only to a minimal increase in the excited state lifetime (i.e. for 54, the detected lifetime
changed from 6.14 to 7.60 ns, Fig. 70a). This behavior suggests that triplet excited states are not involved in the fluorescence emission of these compounds, and no TADF but only fluorescence was observed.

In contrast, the excited state lifetime of the remaining chromophores was strongly affected by the removal of air. For these compounds, under degassed conditions, two decay regimes were observed (Fig. 70b). The first component was associated with lifetimes in the nanoseconds range, whereas the second yielded lifetimes in microsecond time range with values that spanned between 1.18 μs to 97.9 μs which were recorded for compound En-69 and 55, respectively. The fast, prompt component could be observed under aerated conditions, while the long, delayed component disappeared in the presence of air.

The long decay regime detected under degassed conditions strongly indicated the involvement of triplet excited states in the emission process. Additionally, the emission profile did not change significantly upon removal of air, indicating that the prompt and delayed components originate from the same excited state. These two elements led us to assume that, under degassed conditions, part of the emission of all compounds except for 50, 53 and 54 indeed occurs via TADF.

The observation of two decay regimes in the absence of air can be explained with the same mechanism already reported for the other DA-TADF emitters presented in the introduction (chapter 1.3). The fast component, or prompt fluorescence, is generated by the radiative decay of the molecules that, upon photoexcitation and subsequent electron transfer, directly populated 1CT. This process is also observed in the presence of air since it does not involve the participation of triplet excited states; the lifetime associated with this emission is only subjected to a marginal change under the two conditions. The delayed component, or delayed fluorescence, is instead generated by the molecules that populate 3CT. The molecules in these excited states cannot undergo direct radiative relaxation to the ground state due to the forbidden nature of the transition. However, the spatial separation of the HOMO and LUMO orbitals caused 1CT and 3CT to be close in energy. The molecules in 3CT can therefore undergo up-conversion to 1CT by taking advantage of the thermal energy of the environment and subsequently radiatively decay from the singlet excited state. From this description, it follows that the emission of the molecules that populate 1CT via this pathway is clearly identical to the one of the prompt fluorescence. However, the different kinetic of the thermally activated process compared to the direct excitation to 1CT
causes its related emission to be delayed compared to the prompt fluorescence. The involvement of triplet excited states in the mechanism as the base of the delayed emission causes this process to be readily quenched by the presence of air, making it easily distinguishable from the prompt emission. However, it must be noted that the reported description is highly simplified and that in the TADF process, the excited state localized on the donor or acceptor moiety also plays an important role. A more detailed explanation of the phenomena is provided in the introduction of this thesis (chapter 1.3.1.2).

The observation of TADF for only a part of the synthesized compounds may depend on several factors due to the complex nature of the TADF emission. All the compounds that did not show a delayed emission have a nitrogen-based donor unit. This would suggest that the heavier sulfur atom could promote the delayed fluorescence by increasing the spin-orbit coupling between 1CT and 3CT, which would facilitate the rISC between the two excited states. However, the presence of the sulfur heteroatom could not be the only factor influencing the TADF performances since both compounds 36 and 52 include a nitrogen-based donor unit and displayed, under degassed conditions, a delayed decay component. Most probably, the lack of TADF is more connected to the low energy related to the 3CT-0S transitions. As already reported by other authors, the development of efficient red- and infrared-TADF emitters is particularly challenging because of the competition between non-radiative and radiative relaxation pathways, which significantly affect these low-energy emitters.\textsuperscript{126, 227} Adachi and co-workers additionally analyzed two different families of TADF emitters and showed that the rate for the internal non-radiative deactivation pathways of the triplet states is inversely proportional to the energy of singlet excited state, in accordance with the energy gap law.\textsuperscript{228} Therefore, it is highly probable that for compounds 50, 53 and 54, the non-radiative relaxation of 3CT prevails over the conversion of this state to 1CT via rISC. As discussed later in chapter 3.4.1.2.4, we hypothesize that non-radiative relaxation processes may play an important role for this class of emitters and particularly influence the quantum yield of the chromophores in solution. It is, therefore, plausible that other processes that are strongly affected by this phenomenon are also additionally hindered. This hypothesis is supported by the observation of a long decay component for 53 when the compound was embedded in a polymeric thin film (chapter 3.4.1.4). Under these conditions, the restraints induced by the matrix suppress the competing non-radiative relaxation process, thus favoring the rISC base upconversion.

The excited state lifetimes associated with the delayed component of the transient decays ranged between 1 and 3 μs for most of the examined emitters. However, compounds 55 and En-59 represented an exceptional case and yielded the values of 97.9 μs and 51 μs, respectively. The result obtained for compound En-59 can be motivated by the presence of the bromine atom in the molecular structure (see later in chapter 3.4.1.2.3.1). On the other hand, pinpointing a single cause for the exceptionally longer lifetime recorded for compound 55 proved to be complicated. The atypical result obtained for this chromophore may be connected to the higher rigidity of the benzo[h]quinoline fragment compared to the other acceptor moieties. As already reported for other TADF emitters, an excessive structural rigidity renders the vibronic coupling between the local and the charge transfer excited states less efficient, reducing the rISC rate and therefore increasing the lifetime of the triplet states.\textsuperscript{78, 229} The same effect, however, could not be observed for compound 53 which contains the same acceptor moiety of 55. Compound 53 did not show any delayed fluorescence in degassed toluene solution and, when embedded in polymeric thin films, the excited state lifetime associated with its delayed component was in line with the one observed for the other chromophores. It could not be excluded that the unusual behavior of compound 55 may be produced by a misalignment between LE and CT on the energy scale. As previously
mentioned, it had been shown that locally-excited states play an essential mediator role in promoting the rISC process and consequently the TADF emission. Therefore, together with $\Delta E_{3T}$, the energy of locally-excited states must also be considered when interpreting the rate of the delayed emission. A big energy difference between LC and CT would hinder the mediator role of LC and cause a decrease of $k_{rISC}$ leading to an increase of the excited state lifetime associated with the delayed emission. Another element that could play an important role in determining the photophysical properties of compound 55 is the presence of the sulfur atom at the donor moiety. As reported in different studies, the incorporation of a sulfur heteroatom can influence both $\Delta E_{3T}$ and the rates of ISC and rISC.\textsuperscript{172, 173}

Many interwoven factors determine the photophysical properties of a TADF emitter; therefore an appropriate explanation for the remarkably long excited state lifetime displayed by compound 55 can only be formulated after executing a dedicated study. More experiments with compound 55 had been performed with the emitter embedded in a polymeric thin film and are described in chapter 3.4.2. Nonetheless, the elements collected thanks to these additional measurements did not allow to draw definitive conclusions. Calculation of the energy level of the various orbitals involved in the delayed emission and the rate constants of the various transitions would help draw a precise picture of the dynamic involved in the emission of this chromophore.

3.4.1.2.3.1. Excited state lifetime and halogen atoms

The significant change in the excited state lifetime observed for compound En-59 compared to the unsubstituted chromophore 56 is clearly connected to the installation of the bromine atom at the donor moiety. The excited state lifetime associated with the delayed component in the transient decay of the brominated emitter is 34 times longer than the one of the parent structure with the measured values accounting for 1.5 $\mu$s and 51 $\mu$s for 56 and En-59, respectively. In contrast, the derivatization of the donor moiety with other residues caused a much smaller change in the lifetime of the delayed emission. Compounds Di-65 and En-71 delivered the higher values of 2.4 $\mu$s and 2.45 $\mu$s, respectively, whereas compound En-69 delivered the lower value of 1.18 $\mu$s. Fluorination of the acceptor fragment was also shown to influence the lifetime of the excited state but with the opposite effect compared to the bromination of the donor. The delayed component of the excited-state decay for compound 36 showed a lifetime which is almost two times longer than the one measured for the fluorinated compound 52 (2.8 $\mu$s against 1.5 $\mu$s). A similar effect was observed by Shiu, Chen, et al. when comparing the photophysical properties of their mono- and di-fluorinated TADF emitters.\textsuperscript{103}

The effect on the photophysical properties of TADF emitters of the inclusion of halogen atoms in the molecular structure had already been covered in some previously published works.\textsuperscript{29, 88, 103, 230-233} An important differentiation must be made between the introduction of fluorine and the functionalization of the chromophore with heavier halogen like chlorine and bromine. Even though the introduction of fluorine or the heavier halogens may influence the lifetime of the triplet excited state in the same fashion, they act on different parameters and mechanisms of the system.

All the studies involving the introduction of chlorine or bromine in the molecular structure of TADF emitters pointed out how the presence of a heavier atom increases the spin-orbit coupling and therefore accelerates the related ISC and rISC processes.\textsuperscript{29, 231, 233} In DA-TADF emitters, an increase of $k_{rISC}$ is typically associated to a faster decay of the delayed component and, therefore a shorter lifetime of $3^1$CT. Accelerating the conversion of $3^1$CT reduces the involvement of the triplet excited states in bimolecular quenching processes, which usually leads to higher efficiency for the delayed fluorescence. As mentioned
in chapter 1.2, a general reduction of the excited state lifetime is also beneficial for OLED applications since it improves the emitter’s stability, thus reducing the device efficiency roll-off. Interestingly, introducing a bromine atom at the donor fragment of compound 56 led to an increase of the lifetime associated with the delayed component of compound En-59 and therefore to a general extension of its excited state decay.

As shown by some published studies, the introduction of a heavy atom in the structure of TADF emitters does not always cause a reduction of the excited state lifetime. An increase in the spin-orbit coupling influences, in fact, both $k_{\text{rISC}}$ and $k_{\text{isc}}$. By comparing the data reported in different studies, it can be seen how the addition of a bromine or chlorine atom in the molecular structure causes a reduction of $^3\text{CT}$ lifetime only in emitters that display a low value of $\Delta E_{\text{ST}}$. For instance, the emitters reported in the works of Xiang et al. and Kretzschman et al. displayed $\Delta E_{\text{ST}}$ values between 0.04 and 0.08 eV, and the introduction of a bromine or chlorine atom in the molecular fragment led to a decrease of the excited state lifetime.\textsuperscript{29, 231} A different outcome is observed for emitters with a greater $\Delta E_{\text{ST}}$. The chromophores developed by Gu, Han, et al. displayed values of $\Delta E_{\text{ST}}$ between 0.24 and 0.35 eV.\textsuperscript{233} In this case, incorporating a bromine atom in the molecular scaffold led to an increase in the lifetime associated with the delayed component. This result may be attributed to a much more significant increase of $k_{\text{ISC}}$ than $k_{\text{rISC}}$ due to the high energy difference between the singlet and triplet states which ultimately favors the exergonic ISC process. Translating the reported observation to our system leads us to hypothesize that introducing the bromine atom causes a greater increase of $k_{\text{ISC}}$ than $k_{\text{rISC}}$ due to a relatively large value of $\Delta E_{\text{ST}}$. However, it is necessary to experimentally derive the characteristic rate constants and the energy of the involved orbitals to confirm this hypothesis. Additionally, $\Delta E_{\text{ST}}$ is, most likely, not the only factor that must be considered in this context. The efficiency of the fluorescence emission and the non-radiative processes also determines the lifetime of the excited states and are strongly connected to the rISC and ISC processes. The limited number of dedicated and detailed studies on this topic and the lack of an in-depth study of compound 56 did not allow to draw more precise conclusions.

All the above-mentioned studies showed how the triplet excited state’s lifetime is directly connected to the stability and efficiency roll-off of the devices in which the emitters were employed. The OLED based on the brominated emitter with a longer $^3\text{CT}$ lifetime displayed a much faster device degradation than the one based on the not-brominated emitter. Conversely, the devices containing the brominated or chlorinated emitter developed by Xiang, Zaho et al., with a decreased $^3\text{CT}$ lifetime, displayed a lowered external quantum efficiency roll-off. From the reported observations, it could be concluded that bromination of the donor moiety of 56 cannot be used to improve the performances of these molecules in OLED devices.

Rather than influencing the spin-orbit coupling of the system, the introduction of fluoride substituents was shown to decrease the energy gap between the singlet and triplet excited states.\textsuperscript{103, 232} The reduction of $\Delta E_{\text{ST}}$ has a higher impact on the endergonic rISC, ultimately leading to a reduction of the triplet excited state lifetime. Jiang, Marder, and co-workers had additionally reported that upon the inclusion of the fluorine atoms in their system, the yield of prompt fluorescence decreases as an effect of the reduced oscillator strength. At the same time, however, the total photoluminescence quantum yield increased because of the enhanced $k_{\text{rISC}}$. Therefore, the introduction of fluoride substituents can be an effective way to minimize the $\Delta E_{\text{ST}}$ without sacrificing the efficiency of the emitter. The observations concerning the excited state lifetime are in line with the data obtained from the comparison between compound 36 and the fluorinated analog 52. However, the photoluminescence quantum yield of the two
emitters embedded in PMMA polymeric thin films did not show a significant difference (chapter 3.4.2). Compound 52 yielded even a slightly lower value of 28% compared to the value of 33% measured for compound 36. As already mentioned, reducing the 3CT lifetime is one way to reduce the efficiency roll-off of the devices in which the chromophore is embedded. Shiu, Chen et al. showed that the fluorination of their emitters led, indeed, to an increased device stability. A comparative study with compound 36 and 52 incorporated in devices should be therefore performed to judge whether fluorination of the acceptor moiety leads to device with a diminished efficiency roll-off also for this family of compounds.

3.4.1.2.4. Fluorescence quantum yield

Either in the presence or in the absence of oxygen, the measurements of the photoluminescence quantum yield (PLQY) of the examined emitters delivered low values, never exceeding 5%. This result is clearly inferior compared to the values of 100%, 39.2% and 44.4% obtained for the related compounds 27, 29 and 31, respectively, synthesized by Wu, Chi, Chou and co-workers (Fig. 23). Against our predictions, using a bidentate ligand at the acceptor and adopting a donor-spiro-acceptor architecture did not improve the emitters’ photoluminescence quantum yield but led, instead, to a significant worsening of this property. We hypothesized that the low PLQY values might be connected to the flexibility of the donor moiety and the two different conformations that this fragment can assume, as illustrated in chapter 3.3.2. The rapid interconversion between the two conformers could lead to the dissipation of the excited state energy via non-radiative processes, drastically reducing the efficiency of the radiative process.

In DA-TADF emitters, a small overlap between the frontier orbitals is needed to achieve a small energy difference between 1CT and 3CT. However, the small overlap between the two orbitals also reduces the fluorescence’s oscillator strength and, consequently, the fluorescence decay rate. A slower fluorescence emission increases the probability of a non-radiative decay and makes the excited state more vulnerable against bimolecular quenching processes (see chapter 1.3).

Due to the many factors that interplay in the emission via thermally activated delayed fluorescence, a dedicated study like the one performed by Nobuyasu, Ward et al. or by Kukhta et al. needs to be performed in order to isolate the effects produced by the flexibility of the donor on the emission. A flexible structure does not only imply the possibility of energy dissipation through vibrations or conformational changes. For example, Kukhta et al. showed that the different conformations assumed by their flexible donor also dictate the geometry of the heteroatom’s lone pair determining the donor strength of the same fragment. These different conformations influence, in turn, the CT formation and, subsequently, the TADF efficiency. It must also be noted that Nobuyasu, Ward et al. showed that an excessive rigidity is not beneficial for the TADF emission since it may prevent molecular reorganization, which would slow down the initial electron transfer step and the emission from 1CT. As remarked by Penfold et al., TADF relies on a spin-vibronic mechanism, where the nonadiabatic coupling between CT and LE and, therefore, a certain degree of molecular flexibility is needed.

The influence of temperature on the emission of compound 56 was examined to gain more insight into the factors influencing the compounds' PLQY. Cooling down at different temperatures, a degassed solution of compound 56 yielded fluorescence spectra with increasing intensities as the temperature diminished (Fig. 71). This result contradicts the expected behavior of TADF emitters which usually display a decrease of the emission intensity at lower temperatures since the upconversion from 1CT to 1CT is a thermally promoted process. A drastic change in intensity and a marked shift of the emission maximum was observed when the temperature changed from -80 °C to -95 °C (freezing point of toluene).
The drastic change in intensity can be attributed to the fact that, at this temperature, the solution has reached its freezing point, and, in the frozen solution, the molecular motion is highly restricted. It can be assumed that, under these conditions, the interconversion between the different conformations of the donor fragment is not possible anymore. In the frozen solution, non-radiative processes are strongly inhibited, leading to an increase in the emission intensity. The blue-shift of the emission maximum is possibly caused by the limited possibility of the frozen matrix to reorganize and, therefore, stabilize the polar excited state. The inclusion of the emitter in a polymeric thin film should lead to a similar inhibition of the conformational changes at the donor moiety and deliver a comparable outcome. Indeed, under these conditions, the emission intensity of most emitters increased, as described in a more detailed manner in chapter 3.4.2.1. Additionally, for compound 56 the emission spectrum of the frozen toluene can be almost perfectly superimposed with the emission profile of the same compound embedded in a PMMA thin film (Fig. 72). This first experiment would suggest that molecular flexibility indeed plays a significant role in determining the efficiency of the fluorescence emission of the examined emitters. Further experiments and suitable modifications of the donor moiety are, however, necessary to confirm this hypothesis.
Fig. 72 comparison of the emission spectra of compound 56 in a frozen toluene solution (dashed line) or in polymeric thin

<table>
<thead>
<tr>
<th>Compound</th>
<th>ε (10^4 L cm⁻¹ mol⁻¹)</th>
<th>Stokes shift (cm⁻¹)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; Emission (nm)</th>
<th>τ under air (fractional intensities)</th>
<th>τ under vacuum (fractional intensities)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>1.4701</td>
<td>14,653</td>
<td>599</td>
<td>41.6 ns</td>
<td>91 ns (75); 2.8 μs (25)</td>
</tr>
<tr>
<td>50</td>
<td>1.2304</td>
<td>18,298</td>
<td>627</td>
<td>19 ns</td>
<td>53 ns</td>
</tr>
<tr>
<td>51</td>
<td>1.0014</td>
<td>13,456</td>
<td>526</td>
<td>27.5 ns (64); 259 ns (36)</td>
<td>35 ns (16); 2.7 μs (84)</td>
</tr>
<tr>
<td>52</td>
<td>1.4245</td>
<td>15,291</td>
<td>604</td>
<td>23 ns</td>
<td>110 ns (82); 1.5 μs (18)</td>
</tr>
<tr>
<td>53</td>
<td>0.4819</td>
<td>11,561</td>
<td>662</td>
<td>14.1 ns</td>
<td>21.5 ns</td>
</tr>
<tr>
<td>54</td>
<td>1.0059</td>
<td>13,039</td>
<td>730</td>
<td>6.14 ns</td>
<td>7.60 ns</td>
</tr>
<tr>
<td>55</td>
<td>0.5093</td>
<td>9,123</td>
<td>570</td>
<td>3.23 ns</td>
<td>97.9 μs&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>56</td>
<td>1.1344</td>
<td>10,459</td>
<td>617</td>
<td>11.3 ns (50); 86 ns (50)</td>
<td>22 ns (10); 1.5 μs (90)</td>
</tr>
<tr>
<td>57</td>
<td>2.3180</td>
<td>10,421</td>
<td>683</td>
<td>1.42 ns</td>
<td>1.47 ns (98); 14 ns (2)&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>En-59</td>
<td>-</td>
<td>10,028</td>
<td>601</td>
<td>2.6 ns (17); 97 ns (83)</td>
<td>2.84 μs; 51 μs&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Di-65</td>
<td>-</td>
<td>9,944</td>
<td>598</td>
<td>10.8 ns (45); 105 ns (55)</td>
<td>15 ns (5); 2.4 μs (95)</td>
</tr>
<tr>
<td>En-71</td>
<td>-</td>
<td>10,273</td>
<td>610</td>
<td>11.1 ns (43); 104 ns (57)</td>
<td>18 ns (5); 2.45 μs (95)</td>
</tr>
<tr>
<td>En-69</td>
<td>-</td>
<td>10,872</td>
<td>636</td>
<td>12.3 ns (48); 92 ns (52)</td>
<td>21 ns (12); 1.18 μs (88)</td>
</tr>
</tbody>
</table>

Table 4<sup>a</sup> The energy difference was measured between the absorption peak closest to the absorption onset and the emission maxima, <sup>b</sup> The sample were excited at a wavelength corresponding to the absorption maxima closest the absorption onset, <sup>c</sup> sample excited with a photodiode emitting at 320 nm unless otherwise specified, <sup>d</sup> sample excited with a flash lamp at the same wavelength used to register the emission spectra, <sup>f</sup> sample excited with a laser emitting at 405 nm.
3.4.2. Measurements in doped polymer matrices

The photophysical properties of the emitter embedded in polymeric thin films are highly relevant for TADF emitters since the application of such chromophores in OLED devices implies the inclusion of the fluorophores in solid-state thin layers. Moreover, as reported by Bryce and co-workers\cite{Bryce2012}, in the solid-state, the equilibrium between different conformers is constrained. Under these conditions, we could therefore exclude the rapid interconversion between the donor moiety’s conformations from the factors influencing the emission. Generally, the photophysical properties recorded using polymer matrices can also be considered free of any intermolecular contributions since the molecules are spaced out by the matrix. The polymer used for the fabrication of the thin films was poly-(methyl methacrylate) (PMMA). As a term of comparison, also the cyclo-olefin polymer ZEONEX® was tested for some chromophores. Different studies highlighted, in fact, the existence of a significant dependency of the emitter’s photophysical properties from the matrix polarity.\cite{Bryce2012a,Bryce2012b} A list of the more relevant photophysical parameters obtained from the measurements of the examined thin films are reported in Table 5.

PMMA thin films of the compounds with a phenylpyridine acceptor were fabricated by spin-coating a DCM solution containing the polymer and the emitter on quartz plates. Incorporating the emitter in the polymeric matrix typically suppresses the interaction between the chromophores and oxygen. Therefore, the measurements concerning these thin films were performed under atmospheric conditions. Surprisingly, the emission of the thin film containing compound 55, prepared following the above-mentioned procedure, showed to be quenched entirely if the thin film was exposed to air. For this reason, the PMMA and ZEONEX® thin films of the compounds with an extended π system at the acceptor unit were produced differently. Such films were fabricated by covering the inner surface of an NMR tube with the polymer-emitter solution and subsequently evaporating the solvents under vacuum. The tubes were then flame sealed under vacuum. A thin film of compound 51 was fabricated with both techniques to quantify the influence of the two different manufacturing processes on the photophysical properties. The analysis of both thin films yielded comparable results in terms of quantum yield; the lifetimes of the excited state slightly increased in the sample under vacuum but remained in the same time range.

3.4.2.1. Fluorescence emission and quantum yield

The emission peaks observed in the polymeric matrices were all blue-shifted compared to the one recorded for the toluene solutions. This shift to higher energy may be attributed to the lower reorganization capability of the polymeric matrix compared to the one of the liquid organic solvent. The reduced ability of the polymer’s molecules to move and reorganize around the emitter leads to a less efficient stabilization of the excited state and consequently to a shift of the emission to higher energy values. Changing the polymeric matrix from PMMA to ZEONEX® also caused a shift of the emission maxima, but the direction of the shift proved to be compound-dependent. Namely, a shift toward lower wavelengths of the emission was observed for compounds 53 and 55, which both incorporate a benzo[h]quinoline-based acceptor. On the contrary, the emission maxima of compounds 54 and 56, which contain a 2-phenylquinoline-based acceptor, displayed a shift towards longer wavelengths.

We could not find a logical connection between the kind of acceptor moiety present in the structure and the different behavior observed upon exchange of the polymeric matrix. Nonetheless, varying the relative strength of the donor or acceptor fragments leads to the same trends observed for the emission in solution. Namely, an increase of the donor or the acceptor strength causes a bathochromic shift of the
detected emission. The only significant difference that could be observed was that, in solution, compound 56 emitted at a lower wavelength with respect to compound 53, whereas the opposite situation was observed for the thin films emissions.

The photoluminescent quantum yields values displayed by the chromophores embedded in the polymeric matrix were significantly higher than the ones observed for the solution measurements. This effect, observed for other highly flexible emitters, is most likely connected to an enhancement in the fluorescence and TADF quantum efficiency induced by the incorporation of the emitter in the rigid polymeric environment, which suppresses the non-radiative processes.\textsuperscript{240} The maximum quantum yield value of 35\% was recorded for compound En-71 whereas, the lowest value of 3\% was measured for compound 54. Exceptionally, compound 57 did not display a measurable emission when embedded in the polymeric matrices. It must be noted that even though the photoluminescence quantum yields radically increased under these conditions, the relatively low absolute values suggest that non-radiative processes still dominate over radiative decays.

Compound En-71 displayed a remarkable two-fold increase of the photoluminescent quantum yield compared to the unsubstituted parent compound 56. Specifically, the PLQY values of compounds 56 and En-71 accounted for 16\% and 35\%, respectively. This unexpected result showed that derivatization of the donor moiety might not cause drastic changes to the observed emission wavelength, but it could still be used as a powerful tool to improve the efficiency of the emission process. The increase in luminescence quantum yield of compound En-71 may be connected to an increase of $k_{\text{ISC}}$, which would render the triplet excited state less prone to undergo non-radiative deactivation, increasing the efficiency of the radiative processes. This hypothesis is supported by two observations, a reduced lifetime of the delayed component (15.1 $\mu$s for En-71 and 60 $\mu$s for 56) and an increase of the delayed component’s fractional intensity (51\% for En-71 and 15\% for 56). These two parameters together demonstrate that the triplet excited states contribute remarkably more to the fluorescence of compound En-71 than in the unsubstituted compound. However, further experiments are needed to confirm this hypothesis and identify the exact role of the substitution in this meliorative change. Observing a higher quantum yield for the compound with a substituted donor also motivates the synthesis of chiral emitters via the strategy reported in chapter 3.2.

![Image of thinfilms doped with 5 wt% emitter illuminated with UV light. From left to right, emitter 51, 55, 53, En-71, 56 and 54.](image.png)
3.4.2.2. **Excited state lifetime and spontaneous exciton formation**

The photodiode emitting at 320 nm was used as the pulsed source for the TCSPC measurements of the phenylpyridine-based emitter since its emission was reasonably close to these compounds' absorption onset. For compounds 53, 54, 55 and 56 the lack of a laser or diode with a wavelength close to the absorption onset brought us to test the xenon flashlamp as pulsed excitation source as the first option. In contrast to the measurements performed in solution, the pulse provided by this source proved to be shorter than the decay process, and the xenon flash lamp was therefore used as the excitation source for the TCSPC measurements. Using this light source was particularly advantageous since the excitation wavelength could be easily selected and precisely adjusted to the absorption onset by acting on the excitation monochromator.

The excited-state lifetimes recorded for the emitters in the polymeric matrixes were longer than those obtained for the measurements in solution, and the magnitude of the increases was highly compound-dependent. For all compounds except 54 and 57, two different components in the microsecond range were observed. As previously discussed for the measurements in solution, the two components could be assigned to the prompt and the delayed fluorescence emission, implying that all compounds displayed TADF when embedded in a polymeric thin film except for 54 and 57. As already mentioned in the previous chapter, the fact that compounds 50 and 53 displayed a delayed component in the polymeric matrix but not in solution may be linked to the low energy associated with their emission. According to the energy-gap law, fluorophores with a more red-shifted emission are more likely to follow non-radiative relaxation pathways. Therefore, it is reasonable that the TADF emission of these chromophores is favored by the more rigid environment that limits molecular vibration and thereby suppresses non-radiative relaxation processes. The strong competition between non-radiative and radiative relaxation processes for molecules with a low-energy emission undoubtedly plays a significant role in the absence of a delayed component and a low PLQY for compound 54, which displayed the emission with the lowest energy among all examined thin films. On the other hand, the complete absence of emission for compound 57 is puzzling since the emitter displayed a weak but detectable fluorescence emission in solution.

Except for compound 55, the transient decays of the ZEONEX® thin films yielded shorter excited state lifetimes than the one recorded for the PMMA thin films. This difference may be connected to the different polarities of the two polymeric matrices. ZEONEX® is, in fact, less polar than PMMA and can therefore provide less stabilization to the polar charge-transfer excited state. This hypothesis is, however, not supported by the shift of the emission maxima. In analogy to the influence of the solvent polarity on this parameter, we would expect a consistent blue-shift of the emission maximum when ZEONEX® is employed instead of PMMA. As previously reported, however, the direction of this shift was different depending on the compound considered.

A consequence of the faster decays displayed by the ZEONEX® thin films is that the IRF of the flash lamp occupied a significant part of these transients. This aspect made using a tail-fit procedure less adequate for the extraction of the excited state lifetimes. Using the lamp IRF in the deconvolution procedure could solve the problem of interpreting these decays but may not deliver an accurate description of the initial part of the transient due to the impossibility of keeping the pile-up rate below 10% (The results delivered by both methods are reported in the appendix section). As a result of these considerations, we decided to perform a comparative study between the two pulsed excitation sources,
flash lamp and photodiode, using the ZEONEX® thin films. The TCSPC measurement of the ZEONEX® thin film of compound 51 was performed using both pulsed sources and yielded the decays depicted in (Fig. 74).

The TCSPC measurements delivered two valid decays that, however, evolved over two radically different time scales and yielded significantly different excited state lifetime values. It could be excluded that the baseline observed in the measurement with the photodiode corresponds to a residual longer emission since the same noise level was obtained when the measurement was performed with the light source disabled. The two decay segments are again reported in Fig. 75, using a logarithmic scale on both axes and without the initial part influenced by the emission of the flash-lamp, known as instrument response function (IRF). The blue traces correspond to the emitter transient decay.

This phenomenon had already been reported in the literature for other TADF emitters, and its origin is attributed to a difference in the type of mechanism responsible for the generation of the excited states.241, 242 Specifically, the direct photoexcitation of the emitter and exciton recombination. The first mechanism is the standard way excited states are generated upon irradiation. The second mechanism implies the prior spontaneous generation of exciton in the doped polymeric matrix and proceeds as follows. Firstly, a photo-induced charge-separation process leads to the generation and accumulation of relatively long-lived carriers; the photo-generated excitons successively recombine, generating singlet and triplet excited states. Adachi and co-workers first observed and reported this process in 2019, followed by few other research groups.241, 242 One of the methods used by the authors to detect this phenomenon was indeed the analysis of the trend followed by the transient decay. As reported in the published works, the formation of excited states via direct light excitation would yield a classical exponential decay whereas, if the excited states are produced by exciton recombination, a power-law trend was observed.
The proposed mechanisms for spontaneous exciton formation include successive two-photon ionization, charge transfer exciton dissociation, and spontaneous orientation polarization.\textsuperscript{242} It has also been shown that several factors influence the generation of the excitons and therefore the emission via this mechanism. One reported observation which is especially relevant for our analysis is that the carrier formation is proportional to the duration and the intensity of the exciting pulse (\textit{i.e.} Adachi and co-workers could observe such phenomenon only when the exciting pulse was longer than 10 $\mu$s).\textsuperscript{242} The fact that the flash-lamp pulse used in our measurements is significantly longer than the diode pulse (around 75 $\mu$s against 5 ns) would explain how the two TCSPC measurements of compound 51 could deliver the two different transient decays.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig75.png}
\caption{TCSPC decays of compound 51 embedded in ZEONEX\textsuperscript{R} matrix (emitter load 5 wt\%) obtained using two different pulsed excitation sources a) pulsed diode, $\lambda_{exc}$ 320 nm b) flash lamp pulse $\lambda_{exc}$ 375 nm. The initial part of the decays containing the IRF influence are omitted, a logarithmic scale is used on both axes.}
\end{figure}

If the carrier generation occurs via the mechanism of spontaneous orientation polarization the polarity of the host matrix also plays an important role in their formation. Namely, matrices with a higher polarity should facilitate the spontaneous formation of the exciton compared to the less polar one. Such influence might also be observed in our specific case since the TCSPC measurement of the thin films with the apolar ZEONEX\textsuperscript{R} polymer matrix always yielded lower excited state lifetimes than the one of the more polar PMMA thin films. This observation may indicate a lower contribution of the exciton recombination process in the generation of excitons.

By plotting the transient decay of compound 51 embedded in PMMA matrix with a double logarithmic scale, two different regimes can be observed (Fig. 76). In the beginning, the decay follows an exponential trend, and after approximately 0.02 ms, the photon count decreases following a power-law trend instead. This observation suggested that after the 0.02 ms time mark, the excited states are increasingly generated by recombination of the spontaneously formed excitons, thereby confirming the presence of this process also in the PMMA thin films.
Confirming the occurrence of photo-induced charge-separation processes is particularly important since the photoluminescence quantum yield of such a system varies if the excitation source used for the measurements is an optical or electrical source. In the context of this work, this aspect could not be further investigated, and it implies that only data obtained with short excitation pulsed (from a laser or a photodiode) can be considered free from the influence of this phenomenon. Also, only data obtained with a pulse of comparable intensity and length can be directly compared.

3.4.2.3. Detailed analysis of compound 55

In the TCSPC measurements, the thin films of compound 55 displayed the longest excited state lifetime between the examined emitters by a good margin. For this chromophore, the slowly fading of the emission was visible with the naked eye, which made even more evident the difference with the other members of this compound collection. As mentioned earlier, another peculiar characteristic of this chromophore’s thin films was that the presence of air readily quenched their emission. The high sensitivity against oxygen of the emission and its extended lifetime strongly indicates the involvement of a triplet excited state in the radiative decay. However, the unusual photophysical proprieties of compound 55 made us question whether TADF was still responsible for the observed emission or if the luminescence was generated via a different mechanism.

For both the PMMA and ZEONEX® thin films, a suitable interpolation of the transient decays was performed with a biexponential function that yielded two lifetimes both in the millisecond range. However, the biexponential function could be fitted only to the segment of the decay after 1 ms. A function with a higher number of exponentials would be needed to fully interpolate the thin films' transient decay. It must be additionally noted that no TCSPC measurements were conducted using a laser or diode pulse. Therefore, it cannot be excluded that the recombination of spontaneously dissociated excitons influenced the recorded excited state lifetime and that this phenomenon induces the complexity of the observed transient decay. As it can be seen in Fig. 77, the coexistence of an exponential and power-law trend may be observed, especially in the case of the thin film based on ZEONEX®.

Fig. 76 TCSPC decays of compound 51 embedded in PMMA matrix (emitter load 5 wt%) obtained using a flash lamp pulse as excitation source λexc 330 nm. The initial part of the decays containing the IRF influence is omitted, a logarithmic scale is used on both axes.
The non-bell shape for the emission peak of compound 55, both in ZEONEX® and PMMA thin films (Fig. 78), was another unique characteristic that differentiated this emitter from the other chromophores of this series. The peculiar emission profile, together with the remarkably long excited lifetime, made us consider whether more than one process might have been responsible for the emission of this compound, as observed for the emitters described by Bryce and co-workers. In their work, the authors showed how simple variation in the molecular structure could significantly influence the photophysical behavior of an emitter. Thanks to minor structural modifications, they could obtain chromophores that emitted via TADF, room temperature phosphorescence (RTP), or a mix of the two processes. It is also worth noting that some of their emitters displayed TADF when in solution and RTP only when embedded in thin films. The authors attributed this behavior to the inability of the emitter to reorganize its structure upon excitation due to the rigid backbone and the constraints of the polymeric matrix. These two limitations ultimately hindered the population of the charge-transfer excited state and led to the observed peculiar emission. We therefore also consider the possibility that a combination of fluorescence and phosphorescence could be responsible for the emission profile and long persistent luminescence of compound 55.
We firstly analyzed whether a residual emission could be observed in the presence of oxygen. Under normal atmospheric conditions, the thin film displayed only an extremely weak emission that was hardly distinguishable from the instrumental noise and covered the same energy range of the emission under vacuum. The low intensity of the emission did not allow the measurement of a transient decay and a comparison with the same measurement under inert conditions. We then analyzed the dependency of the excited state lifetime with respect to the emission wavelength by measuring a time-resolved emission-spectra (TRES) for the ZEONEX® thin film. The measurement showed that the two detected decay components could be observed throughout the whole emission range with the same relative intensities. As previously mentioned, the analysis did not include the initial part of the decay, and the influence of spontaneous exciton formation cannot be ruled out. Therefore, before drawing definitive conclusions about the emission mechanism for this emitter, it is necessary to perform an analysis that includes the first part of the decay. It is also essential to perform the measurements involving transient decays with a light source characterized by a shorter pulse to exclude spontaneous exciton formation and avoid the interferences of the flash lamp IRF.

Even if they present some critical flaws, these initial experiments did not highlight any inhomogeneity throughout the emission spectra of compound 55. The collected data did not give any indication that the observed radiative decay could be the additive product of a fluorescence and phosphorescence emission. Especially the almost complete lack of any emission under aerated conditions made us consider that room temperature phosphorescence could be at the base of the observed emission. The non-Gaussian shape of the emission profile might not necessarily be induced by the simultaneous contribution of different emission processes. A more defined structure for the emission profile had been observed for other TADF or RTP emitters, and it is caused by a lower vibrational relaxation of the excited state upon excitation.\textsuperscript{42}

To gain further insights into the emission process, we analyzed the influence of temperature on both the emission profile and the transient decay for the ZEONEX® thin film. At values lower than r.t., the emission peak acquired a fine structure that became more defined as the temperature was lowered. At the same time, the onset of the peak shifted to higher wavelengths and became steeper (Fig. 79a). On the
other hand, increasing the temperature of the measurements did not introduce a remarkable change in the emission peak other than a slighter increase of the peak width.

As a term of comparison, the ZEONEX® thin film of compound 56 was subjected to the same low-temperature measurement, and a completely different behavior was observed. As the temperature was lowered, only a slight reduction of the peak width was observed while the emission onset remained unchanged (Fig. 79b). The result of these measurements highlighted a significant difference between compounds 55 and 56 which could only be induced by the different acceptor fragments installed in the structure. The utterly different behavior showed by the two compounds in response to the change in temperature is even more puzzling considering that other properties of the two emitters as the absorption spectra or the emission maxima, are not remarkably different.

The behavior of the transient decay of compound 55, embedded in ZEONEX®, in relation to the change in temperature is reported in Fig. 80. At all the temperatures tested, two different decay components were detected and, as the temperature decreased, the fractional intensity and amplitude of the long component increased as well as the associated lifetime. At 77 K, the duration of the emission’s afterglow did not allow its quantification with the same experimental setup.
Fig. 80 TCSPC measurement at 530 nm for the ZEONEX® thin film of compound 55 at different temperatures. Insert: magnification of the initial portion of the decay. The excited state lifetimes associated to the two detected components at the different temperatures are reported in the legend. In brackets are reported the fractional intensities of each decay component.

The results obtained by this second set of experiments do not contradict the first hypothesis we proposed. However, they could also suggest an alternative mechanism to describe the emission of compound 55. Specifically, it cannot be excluded that the variation of the emission onset and shape caused by the temperature change may be connected to a change of process and excited state involved in the emission. An alternative interpretation of the mechanism behind the observed luminescence could be that, at room temperature, the emission takes place via prompt and delayed fluorescence from a singlet excited state, most likely with a charge-transfer character. Decreasing the temperature would lead to the gradual closing of the TADF channel due to the reduced thermal energy available until, at 77 K, only emission via phosphorescence is observed.

The trend showed by the excited state lifetime could support this hypothesis since decreasing the temperature causes a reduction of the fractional amplitude related to the faster decay component that would agree with the inhibition of TADF. The attribution of a phosphorescence character to the thin film emission of compound 55 at 77 K is supported by its fine structure, typical for this kind of emissions. In the context of this hypothesis, it can also be assumed that the excited state from which the phosphorescence emission takes place is still most likely a charge-transfer excited state. Analogously to what had been reported for the measurements in solution (Fig. 67), we would expect the onset of the phosphorescence emission from locally-excited state to be blue-shifted compared to the charge-transfer fluorescence emission and resemble the emission of compound 83. The comparison between the thin film’s emission spectra at 77 K for compound 55 and 83 indeed showed that the emission onset of compound 83 is much more blue-shifted and does not resemble the emission recorded for compound 55 (Fig. 81).
Fig. 81 comparison of the emission spectra of 5 wt% ZEONEX® thinfilms of compounds 55 (blue line) and 83 (red line) at 77 K.

If we consider that the thin films’ emissions at room temperature and 77 K take place from $^1$CT and $^3$CT, respectively, the energy difference between the onsets of the recorded peaks should provide an estimation of $\Delta E_{ST}$ for compound 55. The difference between the two onsets accounted for 0.32 eV, which is a relatively high value of $\Delta E_{ST}$ for a TADF emitter; however, TADF emitters with $\Delta E_{ST}$ values in the same range have been reported. As repeatedly mentioned in this thesis, to obtain an efficient TADF emitter, the energy difference between $^1$CT and $^3$CT should be minimized so that rISC from $^3$CT to $^1$CT can be achieved using the thermal energy of the environment. Indeed, a low value of $\Delta E_{ST}$ is a sufficient condition for the observation of TADF, but it is not necessary requisite due to the participation of $^3$LE in the rISC process via vibronic coupling. For this reason, also compounds with values of $\Delta E_{ST}$ one order of magnitude greater than the environmental energy can display TADF.

Assuming that the room temperature emission of compound 55 in ZEONEX thin film occurs via the combination of fluorescence and TADF does not provide an explanation for two observations. Namely, the lack of a residual fluorescence emission under atmospheric conditions and an excited state lifetime in the millisecond range. Such long-lived excited states are not commonly observed within the family of TADF emitters which typically display an excited state lifetime in the microsecond range for the delayed component. However, compound 55 would not constitute the first exception to this trend. Indeed, Adachi and co-workers had recently reported a TADF emitter with a remarkably long lifetime of the delayed component. The authors showed that suppressing the spin-vibronic coupling between the $^3$LE and $^3$CT while maintaining a small $\Delta E_{ST}$ leads to a TADF chromophore with a small $k_{rISC}$ and, therefore, an exceptionally long emission lifetime in the millisecond range. The extended lifetime of the emitter causes its emission to be particularly affected by oxygen so that the authors propose oxygen sensing as the possible field of application for the presented chromophore. The emitter presented by the authors displays a similar behavior for compound 55 in solution, whereas no description of the sensitivity against oxygen of its thin films is reported. Therefore, it may be possible that a long-lived TADF emission is at the base of the uncommon emission of 55 embedded in ZEONEX® thin film. Another relevant example is the dopant-matrix system reported by Zhang and co-workers. The emission of this material displayed a TADF-type organic afterglow, its transient decay could be interpolated with two different components in the millisecond range, and the emission’s temperature dependency strongly resembled the one of the
ZEONEX thin film of compound 55. However, the emission of this system was not strongly quenching upon exposing the polymeric thin film to air.

To provide a definitive interpretation of the emission displayed by the thin films of compound 55, further experiments need to be performed. Additional elements can be obtained by calculating the energy of the different excited states involved and examining the initial part of the excited state decay. As already mentioned, it must also be evaluated if and to which extent the slow recombination of spontaneously dissociated excitons contributes to the emission. The measurements of time-dependent emission spectra could also contribute to the interpretation of the emission mechanism. Through these measurements, it is possible to directly visualize the evolution of the emission with time without the need to measure transient decays. The outcome of these experiments should help pinpoint the different stages of the emission process and, therefore, help establish a general interpretation. At last, additional experiments should be performed to exclude that triplet-triplet annihilation plays a significant role in the observed emission (i.e. preparation of thin films with different emitter’s concentration or correlation studies between excitation and emission intensities).

The difference between the photophysical properties of the thin film containing compound 55 and the one containing compound 56 highlight the complex nature of the TADF emission and the many interplaying factors that are at the base of this phenomenon. The dissimilarity between the two chromophores demonstrates the incredible impact of relatively small molecular changes on the photophysical properties of an emitter. Understanding the effect that the different structural changes have on the photophysical properties is decisive since it can be used to modify the emission of these chromophores in a systematic way. This ability would ultimately allow to improve the photophysical performances of these chromophores or modify them according to a precise intent.
### Table 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>PMMA thin films</th>
<th>ZEONEX® thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>QY (%)</td>
</tr>
<tr>
<td>36&lt;sup&gt;b&lt;/sup&gt;</td>
<td>524</td>
<td>33</td>
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<tr>
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<td>492</td>
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<td>25</td>
</tr>
<tr>
<td>57&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>&lt;0.5&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>En-71&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

<sup>a</sup> The sample were excited at a wavelength corresponding to the absorption maxima closest the absorption onset, <sup>b</sup> thin film obtained by spin coating a DCM solution of the matrix and the emitter on a quartz plate, the sample was analyzed under atmospheric conditions, <sup>c</sup> thin-film obtained via evaporation of a toluene solution into a glass NMR-tubes which was then sealed under vacuum, <sup>d</sup> sample excited with a flash lamp at the same wavelength used to register the emission spectra, <sup>e</sup> sample excited with a photodiode emitting at 320 nm.

### 3.4.3. Circular dichroism spectroscopy

The two isolated diastereomers of compound Di-65 were analyzed by means of circular dichroism (CD) spectroscopy. This analysis aimed to evaluate the extent to which the different configurations of the boron chiral center could be detected with this technique. In fact, between the two molecules, only the stereocenter at the boon atom has opposite configurations, whereas the stereocenters of the pinane moiety stay unchanged. As it can be seen in the spectra reported in Fig. 82, the two different stereoisomers yielded two almost perfectly mirrored curves. As can be found in some published examples, the minor differences in intensity and shape between the two spectra are most likely caused by the diastereomeric relationship between the two molecules. A set of two perfectly mirrored curves is expected from this analysis only when a couple of enantiomers is examined.
These measurements show that the different configurations of the stereocenter at the boron atom can be detected by CD absorption spectroscopy. However, this analysis alone is not sufficient to determine the performance of this molecule and its derivatives as a circularly polarized light emitter. For this purpose, analysis via circular polarization luminescence (CPL) emission spectroscopy is needed.

3.4.4. Summary

The measurements performed in these chapters successfully confirmed that most of the sensitized chromophores emit via TADF. As forecasted, the emission originates from a charge-transfer excited state which formation could be achieved thanks to the adopted donor-spiro-acceptor architecture. The charge-transfer nature of the excited state could be proven via the analysis of the emission profile and by analyzing the effect of solvent polarity on the emission maxima. We could also confirm that, due to the high localization of the frontier orbitals, altering the electronic properties of the donor and acceptor fragments affected the energy of the HOMO and LUMO, respectively. This implied that by varying the combination of the two moieties, we could influence the energy difference between the frontier orbitals and consequently the emission wavelength of the chromophores.

The photoluminescence quantum yield of the chromophores measured in solution is remarkably lower than the previously reported emitters without a bidentate donor fragment. We hypothesized that this lower performance is connected to the flexibility of the donor moiety, which with its vibration and conformational changes, can promote non-radiative relaxation processes. This assumption could be partially confirmed by investigating the effect of temperature on the emission intensity and by the fact...
that the Incorporation of the chromophores in a rigid polymeric matrix led to an increase in the observed photoluminescence quantum yield.

Compound 55 displayed a remarkably long-lasting emission compared to the other examined emitters. Additionally, some of its photophysical properties strongly differed from the one of compound 56, which is especially evident if the emissions of the ZEONEX® thin films are compared. With the results delivered by the performed measurements, it was impossible to fully interpret this chromophore’s emission behavior, but thanks to the collected elements, we could suggest that the emission could occur via RTP and or via TADF characterized by a slow rISC.

In conclusion, the photophysical behavior displayed by this family of compounds matched part of our expectations and highlighted the potential of this class of emitters. However, using a bidentate donor fragment did not induce the forecasted improvement of the emitters’ performances compared to the chromophores developed by Wu, Chou, Chi, and co-workers. To systematically improve the performances of this class of emitters and to describe the particular emission of compound 55 in polymeric thin film, a deeper understanding of the emissive process is required. A more detailed study, assisted by the calculation of the energy for the orbital involved in the emissive process, must be performed to achieve a complete comprehension of the connection between the photophysical properties and the structure of the emitter. Nonetheless, the reported study presents a valid foundation for the further development of TADF emitters with this structural motif.
3.5. Cyclic Voltammetry

A selection of the synthesized compounds was subjected to cyclic and square wave voltammetry analysis to investigate their electrochemical properties and to confirm the relationship between the energy associated with their fluorescence emission and the strengths of the donor and acceptor moieties. The cyclic voltammograms of the oxidation and reduction were measured in dry, degassed DCM and THF, respectively. Tetrabutylammonium hexafluorophosphate (0.1 M in the respective solvents) was used as supporting electrolyte and referencing was done against the ferrocene/ferrocenium (Cp₂Fe⁰+/+) redox couple. A summary of the obtained data is reported in Table 6 and Table 7.

![Cyclic voltammograms of compounds 51, 55, 53, 56 and 57 at 400mVs⁻¹. Measurements conducted in 0.1 M Bu₄PF₆ DCM (oxidation) or THF (reduction) solutions. The potentials are referred to the ferrocene/ferrocenium (Cp₂Fe⁰+/+) redox couple.](image)

As it can be seen in Fig. 83, all the examined compounds displayed one chemically quasi-reversible, one-electron oxidation and a non-reversible, one-electron reduction, with the exception of 57, for which two reductive processes were detected within the measurement frame. The oxidation half-wave potentials (E₁/₂ox) for the molecules with a diphenyl sulfide-based donor ranged between 692 and 722 mV. In contrast, the oxidation of compound 53 occurred already at a much lower potential (292 mV), demonstrating that the oxidation is directly related to the installed donor. Additionally, the tendency of the N-methylidiphenylamine-based donor to be more easily oxidized demonstrates that this moiety is a stronger donor compared to the diphenyl sulfide fragment. Similarly, the kind of acceptor moiety installed has an influence on the reduction peak potential (E₀/reduced). The acceptors of compounds 51, 56 and 57 possess an increased number of annulated aromatic rings which translates into an anodic shift in the measured E₀/reduced values. This trend can be again explained by the stabilization of the π* orbitals and the more efficient delocalization of the acquired negative charge produced by the extension of the π system. This observation also confirms that the LUMO of the emitter presents a strong contribution from the π*
orbital of the acceptor fragment. Increasing the size of the aromatic system at the acceptor produces an increase in the acceptor strength, which ultimately lowers the HOMO-LUMO energy gap, as observed in the previous chapter with the analysis of the chromophore fluorescence emissions.

Compounds 55 and 56 delivered $E_{\text{pk \ red}}$ values of -2187 mV and -1963, respectively. The relative position of the two measured values is consistent with the results obtained by the fluorescence measurements of the two emitters, and it confirms that the benzo[h]quinoline fragment constitutes a worse acceptor compared to the 2-phenyl quinoline moiety. An additional difference was also noted between the reduction potential of 55 (-2187 mV) and 53 (-2279 mV), which share the same acceptor fragment. This difference of 92 mV shows that donor and acceptor are not completely isolated and can influence each other to a small extent.

<table>
<thead>
<tr>
<th>compound</th>
<th>$E_{1/2 \text{ ox}}$ (mV)</th>
<th>$E_{\text{onset \ ox}}$ (mV)</th>
<th>$E_{\text{pk \ red}}$ (mV)</th>
<th>$E_{\text{pk \ add}}$ (mV)</th>
<th>$E_{\text{onset \ red}}$ (mV)</th>
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<td>51</td>
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<td>-1963</td>
<td>-1079</td>
<td>-1879</td>
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<td>57</td>
<td>692</td>
<td>597</td>
<td>-2511/-1742</td>
<td>-559,5</td>
<td>-1635</td>
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</table>

*Table 6 Summary of the data obtained from the cyclic voltammetry and square-wave voltammetry analysis.*

$E_{1/2 \text{ ox}}$: half wave potential of the oxidation wave measured at 400 mVs$^{-1}$; $E_{\text{onset \ ox}}$: onset of the oxidation wave recorded via square wave voltammetry analysis; $E_{\text{pk \ red}}$: peak potential of the reduction wave measured at 400 mVs$^{-1}$; $E_{\text{pk \ add}}$: peak potential of the additional wave observed in the reverse scan of the reduction measured at 400 mVs$^{-1}$; $E_{\text{onset \ red}}$: onset of the reduction wave recorded via square wave voltammetry.

By converting the values of the redox-peak onsets, obtained via square wave voltammetry, to the absolute potential scale, it was possible to estimate the ionization potential (IP) and the electron affinity (EA) of the analyzed compounds. For these calculations, the value of 5.1 eV was used as the absolute potential of the couple Cp$_2$Fe$^{0/+}$ in non-aqueous electrolytes. Assuming that the IP and EA are comparable to the HOMO and LUMO energy, respectively, we could estimate the energy difference between the frontier orbitals and compare it to the energy associated with the measured fluorescence emissions (Fig. 84, Table 6). For all compounds, the calculated energy values were lower than the ones associated with the wavelength of the emission maxima obtained via fluorescence spectroscopy. This discrepancy may arise because the electrochemical techniques are based on processes where a net addition or removal of one electron takes place whereas, the formation of the charge-transfer excited state only involves the redistribution of the molecular electron density. Moreover, the emission of the examined compounds is strongly influenced by the polarity of the solvent used for the fluorescence measurements, which further complicates a comparison of the absolute values. More relevant is that the calculated HOMO-LUMO energy gaps follow the same trend of the energies related to the emission in solution, which ultimately confirms the relationship between the emitted wavelength and the donor’s and acceptor’s strength.
The particularly weak or even completely lacking re-oxidation event for the reduction waves had also been observed for the related compounds 27, 29 and 31. In contrast, the compounds reported by Jäckle and co-workers display a chemically reversible reduction. However, these compounds contain the phenylpyridinato boron fragment in a larger conjugated structure and have a methyl group in ortho-position with respect to the pyridyl nitrogen. We hypothesized that the, here observed, lack of reversibility is most probably caused by a follow-up process taking place after the sample is reduced. The detection of a second wave in the anodic scan confirms the generation of another species after the reduction event, supported by the fact that this additional wave could not be detected if the switching potential was higher than that of the reduction of the emitter. A possible explanation for this observation is that the reduction
of the acceptor moiety weakens the coordinative bond between the nitrogen and the boron atom, rendering the boron center more available to further chemical transformations. The complete absence of a reoxidation wave was observed only for compound 53 and 55 even at high scanning speeds. This behavior can be due to the higher rigidity of the acceptor structure and the higher strain to which the five-membered ring containing the boron atom is subjected, rendering the reduced species for these compounds even more unstable.

Additional species could also be detected in the cyclic voltammetric analysis of compound 53 after its oxidation, as it is evidenced by the two peaks at around 5 and -730 mV (Fig. 86). The follow-up process that takes place after the oxidation is possibly slower than the one observed for the reduction. In this case, the backward oxidation wave is not drastically reduced compared to the forward oxidation wave. These additional waves had been observed only for 53 suggesting that the diphenyl sulfide-based donor has higher electrochemical stability than the methyldiphenylamine-based moiety.
Fig. 86 Cyclic voltammogram of compound 53 in DCM at different scan rates.
4. Spiro-C Emitters.

4.1. Synthesis

4.1.1. Introduction

This section describes the development of different synthesis strategies towards the compounds with the general formula 37-R (Fig. 25). The boron atom in this class of compounds is tricoordinate, and therefore its chemical properties are markedly different compared to the boron center found in the chromophores belonging to the class spiro-B. This dissimilarity entailed the adoption of a radically different synthesis approach compared to the one discussed in the previous chapter.

Due to their Lewis acidic nature, trialkyl- and triarylboranes are highly sensitive towards moisture, coordinating solvent, bases, and in general, nucleophiles. These properties render these species typically unstable under normal atmospheric conditions and not compatible with various reactions conditions. For these reasons, in these compounds, the introduction and derivatization of the boron atom usually occur at the end of the synthesis path. However, the stability of triarylboranes can be enhanced by introducing steric protection around the boron atom or by including the boron center in a rigid planar structure (Fig. 87).

Steric shielding is achieved via the functionalization of the boron center with one or more bulky substituents that block the approach of nucleophiles. Commonly employed for this purpose are the mesityl or trisopropylphenyl (tipp) substituents. Conversely, the inclusion of the boron atom in a rigid planar structure leaves the heteroatom exposed. However, a nucleophilic addition would require a rearrangement from a trigonal to tetrahedral geometry, which is hindered by the structural constraints of the stiff structure. It must be noted that both reported methods imply irreversible derivatizations of the boron atom and do not allow the modification of the substituent in a second moment. This work aimed to establish a synthesis procedure towards a common precursor 37-R that could allow further derivatizations at the boron center. Therefore, introducing the boron atom at the beginning of the synthetic path in one of its stable tricoordinate forms was not considered a viable option.

Fig. 87 Molecular structures used to enhance the stability of triarylboranes.

When designing the possible synthesis paths towards 37-R, two main aspects were considered. The stage of the synthesis sequence at which the boron center is introduced and the type of reaction utilized for its installation.

Regarding the stage at which the boron atom is introduced, we examined two elementary alternatives: the introduction of the boron center at an early stage of synthetic path or at the end of the
synthesis sequence. We expected that introducing the boron in the last synthesis stage would simplify the construction of the molecular scaffold since the reactions employed in the preparation of the molecular backbone do not have to be compatible with the presence of the boron center. Instead, if the introduction of the boron atom occurs at the beginning of the synthesis route, the synthesis steps must be developed compatibly to the presence of the heteroatom. In this last case, however, the functional groups or substituents used to introduce the boron center do not need to be present in the structure for the whole synthesis sequence. This aspect may also be regarded as an advantage depending on the synthesis sequence adopted.

Concerning the reaction used to introduce the boron center, the most applied methods in the synthesis of organoboron compounds are the trapping of metalated intermediate with a boron-based electrophile, the tin/silicon-boron exchange reaction, the hydroboration reaction, and transition metal-catalyzed borylations. The tin-boron exchange reaction is nothing but the reaction between a metalated species and a boron-based electrophile. Without dismissing its connection to this reaction macro class, it is worth considering the tin-boron exchange reaction separately and analyzing it with the silicon-boron exchange reaction instead. The two reactions share, in fact, mechanistic details, and the chemo-physical properties of organo-tin complexes render these compounds more similar to their organo-silicon analogs than other metallated species as organolithium and Grignard reagents. The last two mentioned methods, the hydroboration reaction, and transition metal-catalyzed borylations, are not suitable for introducing a borylene bridge into the targeted molecular backbone. In particular, the transition metal-catalyzed reactions allows typically the addition of only one single substituent at the boron center, and the products of the hydroboration reaction are alkylboranes.

4.1.1.1. **Combination of a boron-based electrophile with metalated intermediate**

One of the most employed and long known methods for the synthesis of organoboranes and organoborates is the reaction between a metalated intermediate and an appropriate boron-based electrophile (Fig. 88). This reaction was firstly used by Frankland and Dubba in 1860 for the preparation of triethylborane by reacting diethylzinc with triethylborate.

![Fig. 88 General reaction mechanism of the reaction between a boron-based electrophile and a metalated intermediate.](image)

In this reaction, the metalated species is usually an organolithium or a Grignard reagent, and for the synthesis of alkylboranes, trialkylaluminum compounds are frequently used. In fewer cases, sodium, potassium, calcium, lithium diarylcuprates, cadmium, zinc, and mercury reagents were used. The reactivity of the organometallic reagent increases with the electropositivity of the metal and therefore follows the qualitative reactivity order K > Na > Li > Mg, Al > Cd, Zn > Hg. This trend was verified, for instance, in the work of Gilman and Moore, who showed that cadmium and zinc reagents performed...
worse in the reaction with tri-2-butylborate than the analogous magnesium reagents.\textsuperscript{264} The generation of the Grignard reagent is typically achieved from the corresponding halogenated precursor via direct metatlation with magnesium or \textit{via} transmetatlation with \textsuperscript{1}PrMgCl-LiCl. Organolithium reagents are also generally obtained from a halogenated starting material \textit{via} direct metatlation with Li (for alkyl lithium reagents) or lithium halogen exchange reaction (for aryl lithium reagents). Eventually, also \textit{ortho}-lithiation can be applied if heteroatoms in a suitable position are present, and in these cases, a halogenated precursor is not needed.\textsuperscript{265}

Concerning the boron-based electrophile, boron halides, borates or boranes had been customarily used as the reagent of choice. Haloboranes, especially bromo and iodoboranes, can react with ethers inducing the cleavage of their C-O bond, and therefore care must be taken in the choice of the reaction solvent when these reagents are employed. The reactivity of the boron-based electrophile is directly related to its Lewis acidity and accessibility of the boron atom. For instance, the reactivity of organic aluminum derivatives decreases according to the order BF\textsubscript{3} > BCl\textsubscript{3} > BBr\textsubscript{3} > Bi\textsubscript{3}\textsuperscript{266} The more reactive haloboranes are preferred when sterically demanding substituents are present at the boron center or when homogeneous tri-substitution must be performed.\textsuperscript{267-269} The choice of the substituents at the boron center can be used to tune the reactivity of the electrophile by influencing the steric bulk around the boron atom and modifying its Lewis acidity. Moreover, the nature of the substituents influences the solubility of the generated salts and ultimately influences the equilibria involved in the reaction.\textsuperscript{270}

The reaction between the metalted species and the boron-based electrophile can either directly yield the substitution product or proceed via the boronate salt intermediate \textsuperscript{84} (Fig. 88). The boronate intermediate was mainly observed when lithium or magnesium reagents were used and could also be occasionally isolated.\textsuperscript{271, 272} The reaction solvent also plays a role in the stabilization of this intermediate. As reported by Brown and co-workers, the tetraethylborate complex is preferentially formed in tetrahydrofuran, whereas in diethyl ether, only a few percent of the product was detected.\textsuperscript{273} The stability of this intermediate is particularly important in the synthesis of mixed organoboranes, and therefore dialkyl-arylborinic acid esters or alkyl-diarylboronic acid esters are most frequently used since they form stable boronate complexes.\textsuperscript{274, 275} The displacement of a substituent from the boronate intermediate often occurs spontaneously or by thermal decomposition, especially when boron halides are used. It must also be noted that the eliminated substituent can eventually react with a molecule of the boron-based electrophile and therefore remove part of the boron-based electrophile from the main equilibrium.\textsuperscript{253} In some cases, implementation of a further reaction step is necessary to ensure elimination of the substituent.\textsuperscript{274} In the synthesis of boronic and borinic acids, an acidic aqueous workup with diluted mineral acids is usually performed. In this case, it must also be considered that borinic acids with small organic residues may show high solubility in water, leading to low isolated yields, and therefore isolation of their esters may be preferred. Other frequently encountered procedures for the displacement of the substituent at the boron center which do not imply the presence of water include the use of dry HCl or trimethylsilyl chloride. An example is provided by the synthesis reported in Fig. 89, which was developed in our research group. In this case, after the addition of the electrophile, the alkoxide substituent is not displaced from the boron center. Its extraction is performed by means of the reaction with trimethylsilyl chloride which ultimately yields the final product. In this particular case, the use of aqueous mineral acids was avoided in order to protect the boronate ester from hydrolysis.
Example of reaction in which the elimination of the isopropoxy substituent does not occur spontaneously, and it is therefore performed via the reaction with TMS-Cl.

4.1.1.1. Introduction of a borylene bridge

The introduction of a borylene bridge in the molecular scaffold via the general method illustrated in this chapter implies the adoption of a doubly halogenated substrate, as it is exemplified in the reaction reported by Miao and Cheung (Fig. 90). In the reported example, the bidentate metalated intermediate is generated via a lithium-bromine exchange reaction and then reacted with one equivalent of trimethyl borate. The final product is then obtained after aqueous workup of the reaction mixture.

In general, the chelating nature of the double nucleophile should favor the two-fold substitution on the same boron center, and the careful choice of the reaction condition, as well as the stoichiometry ratios, should also avoid a third attack at the boron atom. The addition of two different metalated molecules to one boron center or of the addition of two different boron electrophile molecules to one molecule of metalated intermediate should be therefore disfavored.

A boron-based electrophile that is particularly useful in the synthesis of borinic acids is diisopropylamino borane. Using this reagent, Pucheault and co-workers could develop a robust method for the synthesis of this class of compounds (Fig. 91).

Diisopropylamino borane is best suited for the reactions with Grignard reagents and delivers poor performances when used in combination with organolithium intermediates. Upon addition of the metallated intermediate to the boron center, the elimination of hydridomagnesium halide is a favored process in contrast to the elimination of lithium hydride and the eliminated HMgX does not react with diisopropylamino borane. In diisopropylamino borane, the donation of the nitrogen lone pair in the empty p orbital of the boron atom reduces the Lewis acidity of the heteroatom which, coupled with the steric hindrance provided by the isopropyl groups, inhibits a third attack at the boron center. Therefore, using this protocol, the product of the double addition at the boron atom is obtained selectively even if the carbon-based nucleophile is used in excess. Another advantage of this method is that the Grignard reagent
can be generated *in situ* in the presence of the electrophile. In the final product, the diisopropylamino substituent can be removed via hydrolysis generating the respective borinic acid.\(^{253}\)

### 4.1.1.2. Silicon/tin boron exchange

Transmetalation reactions of arylstannanes and arylsilanes with boron trihalides are often used in the synthesis of organoboron compounds and offer a valid alternative to the electrophilic trapping of a metalated intermediate. The exchange reaction is performed by the addition of a boron halide to a suitable aryl-stannane or -silane reagent, and the desired transmetalated product is generated together with the organosilicon- or organotin halide as a byproduct. The reaction proceeds through the electrophilic attack of the Lewis acidic boron halide to the carbon atom attached to the silicon or tin center (alpha carbon atom). Depending on the nature of the substrate, two different mechanisms have been observed.

If the alpha carbon atom is sp\(^2\) hybridized and part of an aromatic system, the exchange reaction follows an electrophilic-substitution-type mechanism which is promoted by the electron density of the \(\pi\) bond. The first step of this mechanism includes the electrophilic attack of the boron halide at the alpha carbon atom, leading to the formation of the arenium cation. Subsequently, halogen transfer and the simultaneous cleavage of the carbon-silicon or carbon-tin bond take place (Fig. 92a). Instead, if the alpha carbon atom is sp\(^3\) hybridized, the reaction evolves in a concerted fashion (Fig. 92b).\(^{277}\)

![Diagram](image-url)

*Fig. 92 Possible reaction mechanisms for the boron-tin exchange reaction. a) If the carbon atom connected to the tin center is sp or sp\(^2\) hybridized b) If the carbon atom connected to the tin center is sp\(^3\) hybridized.*

From the discussion of the mechanism, it follows that the transmetalation reaction occurs preferentially at a sp or sp\(^2\) hybridized carbon atom since the electron density provided by the \(\pi\) system facilitates the electrophilic attack. This characteristic can be used to perform regioselective transmetalation reactions. In the first example reported in Fig. 93, only the trimethylsilyl group directly attached to the benzene ring of 85 undergoes boron-silicon exchange generating compound 86, whereas the other trimethylsilyl substituent remains unchanged. In the second example, the boron-silicon exchange reaction takes place preferentially at the sp\(^3\) hybridized carbon of 87, causing a regioselective ring-opening reaction of the heterocycle which yields compound 88.\(^{278}\)
The preference of the exchange reaction to occur on sp or sp\(^2\)-hybridized carbon atoms can be used to perform regioselective transformations.\(^{278}\)

Exchanges involving sp\(^3\) hybridized carbon atoms can also take place. However, they are observed if no more reactive options are available or if structural factors favor this pathway. As reported in Fig. 94, for compound 89 the intermolecular methyl transfer, that yields compound 90, occurs faster than the second boron-tin exchange, and this can be explained by the formation of an intermolecular transition state that competes with the second exchange reaction.\(^{277}\)

If the exchange reaction follows a concerted-type mechanism, steric hindrance is the factor that dictates the regioselectivity of the transformation. As reported by Eisch and co-workers, compound 93 undergoes preferentially exchange of the methyl group instead of the benzylic substituent since this last fragment presents a larger steric hindrance and its participation in the transition state is disfavored. Oestreich and co-workers substituted the two methyl groups bonded to the tin atom with two (trimethylsilyl)methyl substituents in a similar substrate (Fig. 95, compound 95). They then demonstrated that the benzylic position became the favored site for the transmetalation since it showed the fewer steric bulk.\(^{279}\)
Fig. 95 Steric hindrance is the factor that determines the regioselectivity of exchange reactions taking place on sp³-hybridized carbon atoms.\textsuperscript{279}

As it can be deduced from the discussion of the mechanism, the reactivity of the boron trihalide is directly correlated to its Lewis acidity. Boron trifluoride displays the lowest Lewis acidity in this class of compounds and does not react in this kind of transformation. Boron trichloride, tribromide, and triiodide can be used in this reaction, and their reactivity increases from the first one to the latter. Boron tribromide is the halide that is more often used in this reaction since it offers a good balance between reactivity and the reagent cost. Boron trichloride and boron triiodide are less encountered, most probably due to the lower reactivity of the former and high commercial cost of the latter.\textsuperscript{280}

Likewise, in this transformation arylstannanes and arylsilanes show a difference in reactivity which is related to the different bond strengths of the Si-C and Sn-C bonds.\textsuperscript{281} Tin-based starting materials are more reactive than their silicon counterparts; therefore, milder reaction conditions and less aggressive reactants can be normally employed. An elegant example that highlights this difference in reactivity is the selective borylation reported by Jäkle and co-workers (Fig. 96a).\textsuperscript{282} In this reaction, the haloborane in the first and the second attack reacts preferentially with the dimethyltin fragment of compound 97 thereby yielding selectively compound 98. Another consequence of the high reactivity of stannanes in the exchange reaction is that also the less reactive arylated or alkylated boron dihalides can be used. One example of this reactivity is reported in Fig. 96b with the reaction between compound 99 which directly yields the pentafluorophenyl-substituted borane 100 via the reaction with dichloro(pentafluorophenyl)borane.\textsuperscript{283} Even though arylsilanes display a lower reactivity, their greater stability facilitates their synthesis and purification. This factor, together with the high toxicity associated with arylstannanes, makes them the preferred reagent for the exchange reaction. It must also be noted that, for sterically demanding substrates, the smaller dimension of the silicon atom actually facilitates the exchange reaction.
The other two important factors that influence the rate and outcome of the exchange reaction are the partial alkylation of the boron trihalide and the partial halogenation of the silane or stannane. Both modifications reduce the exchange reaction rate and, in some cases, even block the transformation completely. Two examples can be found in the synthesis of the two 9,10-dihydro-9,10-diboraanthracenes 102 and 107 where compounds 101 and 104 represent a dead end in their synthesis, respectively. However, the desired products are obtained if no alkylation of 103 or halogenation of 106 occurs.284, 285

Fig. 96 a) Example of selective borylation, achieved thanks to the different reactivity of Si and Sn in this reaction.282 b) Reaction between a diarylstannane and pentfluorophenylboron dichloride. Arylstannanes easily react also with substituted haloboranes.283
Fig. 97 Partial alkylation of the boron center in compound 101 or partial halogenation of the silicon atom in compound 104 hinders the formation of the corresponding 9,10-dihydro-9,10-diboraanthracenes 102 and 107, respectively.\textsuperscript{284, 285}

The last worth mentioning factor that can influence the outcome of the exchange reaction is the reaction solvent. No dedicated study investigating the role of the solvent and how it can influence the reaction outcome had been published. However, the observation that chlorinated hydrocarbons have an activating effect is frequently encountered in the literature. For instance, compound 108 is converted to compound 109-X under milder conditions when DCM is used as solvent instead of alkanes or to when neat boron trihalide are used.\textsuperscript{278} In a following publication Kaufmann and Gross reported that, when steric hindrance plays an important role, the activation effect of the solvent may also influence the outcome of the reaction. When compound 110 was reacted with neat BBr\textsubscript{3}, the major product of the reaction was the desired borylated biphenyl 112. If the reaction was conducted using chloroform as the solvent, compound 111 was instead the major detected product in the reaction mixture.\textsuperscript{286}
In many works published by Wagner et al., the silicon boron exchange reaction had been successfully employed in the synthesis of a whole variety of organoboron compounds and usually, neat BBr₃ had been employed. In one of their works, it was evidenced that the aromatic hydrocarbons used as solvents may also actively participate in the reaction. In one example, a mixture of hexane and o-xylene was used as the solvent, in the reaction between 115 and BBr₃. Aside from the desired product 116 two other substituted 9,10-dihydro-9,10-diboraanthracenes were also obtained (compounds 117 and 118, Fig. 99). The formation of these last two products could only be explained with the involvement of the solvent in the reaction.

The installation of the tin or silicon atom introduces an additional step in the synthesis sequence, and their introduction typically relies, as it is for boron, on the reaction between a metallated species and an
appropriate silicon or tin electrophile. Nonetheless, the incorporation of the transmetalation reaction in the synthetic sequence still has some advantages. Firstly, the synthetic paths that can be designed using this reaction may not be accessible otherwise. In fact, the silicon and tin atom have a different tolerance towards reaction conditions in comparison to boron. The silicon and the tin atom could therefore be used as a masking group at the beginning of the synthesis path and substituted later with boron. Moreover, the exchange reaction can be used to directly produce halogenated boranes, which are highly reactive and can be derivatized with more straightforward methods. Also, the workup of the exchange reaction is extremely simple since the solvent, the excess boron trihalide, and the volatile tin or silicon halides can be evaporated under vacuum. Alternatively, the byproducts can also be easily removed by washing the obtained material with alkanes.

At last, it is also worth reporting that Helten and co-workers recently developed a catalytic version of the boron-silicon exchange reaction that allows the use of mild reaction conditions without the need of employing organotin reagents (Fig. 100).287

![Fig. 100 Schematic representation of the catalytic B–C coupling by Si/B exchange developed by Helten and co-workers.](image)

The developed protocol allows the exchange of the aryl substituent from an aryl trimethylsilane with the halogen atom of an aryl boron dihalogenide. The process is catalyzed by either Me₃SiOTf or Me₃SiNTf₂.

4.1.1.2.1. Introduction of a borylene bridge

The introduction of a borylene bridge in a molecular fragment via silicon/tin-boron exchange had been previously reported in the literature, and some relevant examples are reported in Fig. 101.288-293 In this particular case, the exchange reaction must occur twice. A first intermolecular exchange must be followed by an intramolecular event to obtain the desired product. As previously mentioned, halogenation of the silicon or tin atom reduces their reactivity in the exchange reaction, potentially leading to the inhibition of the second intramolecular exchange. Analyzing the laboratory procedures of the reported examples shows that the required reaction conditions become harsher as the rigidity of the system increases, but only in rare examples the reaction did not produce the desired product.292
Introduction of a borylene bridge via the silicon-boron exchange reaction reported by Yamaguchi and co-workers (a) and by Wagner and co-workers (b).\textsuperscript{289, 292} Introduction of a borylene bridge via the tin-boron exchange reaction reported Piers and co-workers (c) and Jutzi (d).\textsuperscript{290, 293}
4.1.1.3. *Investigated synthesis strategies.*

The analysis of the available synthesis methods and strategies ultimately led us to pinpoint and investigate three different synthesis approaches, which are schematized in Fig. 102 and that can be summarized as:

- Introduction of the borylene bridge in the molecular scaffold at the last step of the synthesis sequence via electrophilic trapping of a metalated precursor.
- Generation of a boron-based starting material via electrophilic trapping of a metalated precursor, completion of the molecular backbone with reactions compatible with the boron atom.
- Introduction of the borylene bridge via tin/silicon-boron exchange in the molecular structure at the last stage of the synthetic sequence.

The three different approaches are discussed separately in dedicated sections. The last part of this chapter then discusses the purification and derivatization strategies for two precursors obtained via the described methods.

*Fig. 102 Schematic representation of the three different synthesis approaches investigated for the synthesis of 37-R.*
4.1.2. Introduction of the borylene bridge via electrophilic trapping of a metallated precursor at the end of the synthetic sequence

4.1.2.1. Introduction

For the introduction of a borylene bridge via the reaction between a metallated species and a boron-based electrophile, a doubly halogenated starting material is normally employed (chapter 4.1.1.1). We excluded the possibility of generating a twofold lithiated precursor via ortho-lithiation since no directing groups in a suitable position are present in the molecular structure. Therefore, we ultimately targeted compounds 119-Cl and 119-Br as the halogenated precursor (Fig. 103).

![Reaction sequence for the insertion of the borylene bridge in the structure of compound 37-R at the end of the synthesis sequence.](image)

Compound 119-Br had been initially chosen as the starting material for this transformation. Brominated aryls display an intermediate reactivity in the metallation reaction, between the one of chlorinated and iodinated aryls, therefore, offering both a good reactivity and the possibility to easily control the metallation reaction. Additionally, aryl bromides are normally more easily accessible than their iodinated analogs due to the greater availability of starting materials for their synthesis. However, in the course of this work, the synthesis of compound 119-Cl proved to be necessary. This substrate is much less reactive in the metallation reaction than its brominated analog, and the reasons why this compound was ultimately needed will be explained over the course of the following chapters.

Precursors 119-X were synthesized following a modified version of the procedure reported by Adachi and co-workers for the synthesis compound 32 (Fig. 104). The reported reaction sequence consists of only two steps. In the first one, 2-bromotriphenylamine (121) is lithiated using "BuLi and the so generated nucleophile is added to anthraquinone generating compound 122. The spiro center is then generated by acid catalyzed cyclization of the obtained tertiary alcohol. In order to apply the same protocol to the synthesis of 119-X, anthraquinone was replaced with the doubly halogenated benzophenone 123-X (Fig. 104). The synthesis steps towards the halogenated precursor 119-X and compound 37-R are discussed in detail in the following sub-chapters.
Adachi's synthesis:

```
121

1. nBuLi

2. THF

122

CH₃COOH

H₂O

32
```

This work:

```
1. metalation

X = Cl, Br

123-X

124-X

X = Cl, Br

119-X
```

*Fig. 104 Reaction sequence utilized by Adachi and co-workers for the synthesis of compound 32 applied to the synthesis of the halogenated intermediate 119-X.*
4.1.2.2. Synthesis of compound 121

For the synthesis of compound 121 a transition-metal catalyzed cross-coupling between 2-bromoiiodobenzene and diphenylamine was employed. Four different literature-known procedures were tested, and their main reaction parameters are reported in Table 8.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (loading)</th>
<th>Base</th>
<th>Ligand</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(I)(70%)</td>
<td>K$_2$CO$_3$</td>
<td>-</td>
<td>xylene</td>
<td>120°C</td>
<td>48h</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>CuCl(27%)</td>
<td>K$_2$CO$_3$</td>
<td>-</td>
<td>DMSO</td>
<td>165°C</td>
<td>12h</td>
<td>14%</td>
</tr>
<tr>
<td>3</td>
<td>Cu(I)(26%)</td>
<td>NaO$_{t}$Bu</td>
<td>-</td>
<td>THF</td>
<td>65°C</td>
<td>17h</td>
<td>50%</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)$_2$</td>
<td>NaO$_{t}$Bu</td>
<td>xanthos</td>
<td>toluene</td>
<td>100°C</td>
<td>24h</td>
<td>45%</td>
</tr>
</tbody>
</table>

Table 8 Summary of the reaction condition tested for the synthesis of compound 121.

The reactions of the first three entries correspond to a classical Ullman-Goldberg reaction where the base, the reaction solvent, and other reaction parameters were screened. In entry 4, the copper catalyst was replaced with palladium acetate, and a ligand was also used. In terms of obtained yield, the condition of Entry 1 and 2 delivered, in our hands, particularly poor results which were much lower than the one reported in the original publications (70% and 84% respectively). The reaction did not generate byproducts and the crude mixture was solely constituted by the desired product, unreacted diphenylamine, and 2-bromoiodobenzene. The reaction condition of entry 4 delivered the desired product in a much higher yield, but in contrast to the other experiments, carbazole was generated as a byproduct from an Ullman-type intermolecular side reaction. The generation of carbazole was detrimental for two reasons, it reduced the yield of the reaction, and it proved to be particularly difficult to separate from the desired product. The two species could be separated via column chromatography; however, the extremely similar retention times of the two compounds forced the use of over-dimensioned columns. Crystallization did not produce a considerable enrichment in the desired product content, and purification via distillation was not tested. Ultimately, the conditions of entry 3 delivered the best-isolated yield, and no carbazole was generated. This procedure was therefore used for the routine preparation of 121.

![Fig. 105 reaction scheme for the synthesis of compound 121.](image)

The reaction is performed under a nitrogen atmosphere in a closed vessel where the two reactants, the copper catalyst and the solvent are mixed and let react at 65°C for 17h. Purification of the crude mixture was performed either via column chromatography or via Kugelrohr distillation. The distillations procedure can be used to successfully remove the excess of 2-bromoiiodobenzene and isolate the desired product from the high-boiling byproducts but also yields mixed fractions of compound 121 and unreacted diphenylamine. Even though these mixed fractions need to be re-distilled to completely isolate 121, this purification method was still preferable when large-scale syntheses are performed.
4.1.2.3. Synthesis of compound 123-X

Compound 123-Br had been initially synthesized using the two-step reaction sequence reported in Fig. 106, which makes use of the already-brominated starting materials 2-bromobenzaldehyde and 2-bromiodobenzene. The first step of the sequence involved the addition of the in situ generated Grignard reagent 125 to 2-bromobenzaldehyde that yielded compound 126. Using the Grignard reagent 125 instead of the organo-lithium analog allowed to perform the reaction under milder conditions since the lithiated compound undergoes elimination already above -90°C. Pyridinium chlorochromate (PCC) was then used to oxidize compound 126 yielding the desired product, 123-Br in 27% yield over two steps.

![Fig. 106 Two-step reaction sequence for the synthesis of compound 123-Br.](image)

Parallelly, the palladium-catalyzed ortho-selective di-halogenation of benzophenone was also tested for the synthesis of both 123-Cl and 123-Br.

![Fig. 107 Reaction scheme for the synthesis of compounds 123-Cl and 123-Br.](image)

The reaction was conducted following a modified version of the procedure published by Hui Zhang and co-workers who established this procedure for the mono-chlorination of aromatic ketones. The reported protocol could be adapted to the synthesis of 123-Cl by simply increasing the number of equivalents of the halogenating agents NCS. Using this adapted procedure, the doubly chlorinated compound 123-Cl was obtained in 67% yield. Instead, using NBS as the halogenating agent yielded compound 123-Br in 56% yield. Both substitutions occur selectively at the ortho-position with respect to the carbonyl group. This reaction’s high regioselectivity is achieved thanks to the weak coordination of the palladium center to the keto-group, which ultimately leads to the formation of a five-membered palladacycle upon C-H activation. The reaction mechanism supposedly proceeds via a Pd(II)/Pd(IV) catalysis cycle. In the literature, it was additionally shown that the chlorination of benzophenone could also be achieved in the absence of K$_2$S$_2$O$_8$, leaving to NCS the oxidation of the palladium center. However, in the work of Hui Zhang and co-workers, it is highlighted how the use of an oxidant increases the overall yield of the reaction, possibly by increasing the rate of the oxidation step which suppresses the formation of by-products. It is also worth noting that in similar transformations, the oxidizing agent
had been proven essential to the regioselectivity of the reaction, and its absence led to the meta substitution.\textsuperscript{302, 303} TfOH is often used in Pd-catalyzed reactions that exploit weak coordination since the in-situ formation of the electron-deficient palladium complex Pd(OTf)$_2$ can promote more challenging C-H activations.\textsuperscript{304-306}

The palladium-catalyzed pathway yielded the desired products in higher yield than the initial two-step synthesis, and could deliver the desired product in only one stage. Additionally, this reaction did not require inert conditions rendering the whole process to a large extent more practically convenient than the two-step pathway. Considering that both tested synthesis sequences make use of low-cost starting materials, the two-step reaction sequence can be a valid alternative only when the price of the catalyst constitutes a critical aspect of the palladium-catalyzed procedure and when the yield of both steps is considerably improved. Given the amount of starting material needed for this work and the explorative stage of the investigation, we favored the palladium-catalyzed halogenation for the preparation of 123-X.

4.1.2.4. **Synthesis of compound 124-Br**

![Diagram](image_url)

*Fig. 108 Procedure used for the synthesis of compound 124-Br.*

Synthesis of 124-Br was attempted via the addition of compound 123-Br to a solution of the in-situ metallated amine 127-M (Fig. 108). The metalation of 121 could be achieved either using magnesium, and therefore generating the corresponding Grignard reagent, or employing \textsuperscript{9}BuLi and therefore obtaining the lithiated triarylamine. Surprisingly, the addition of 123-Br to both metallated amines did not yield the desired product 124-Br but, instead, the brominated starting material 121. Quenching experiments with deuterated solvents were used to verify the success of the metalation reaction, which confirmed that the organometallic species had indeed been produced. The only conclusion that could be drawn was that the lithium- or magnesium- bromine exchange reaction between 127-M and 123-Br was much more favored compared to the nucleophilic attack at the carbonyl group. We hypothesized that the desired reaction is less favored than the metal-halogen exchange due to the steric hindrance, which protects the carbon atom of the carbonyl group in compound 123-Br. This concept may be better exemplified by analyzing the solid-state structure of this compound (Fig. 109).\textsuperscript{307} Looking at the structure from the vector passing through the carbon-oxygen bond, it is evident that the two aromatic rings need to rotate outside the
carbonyl-group plane to minimize the repulsion between the two bromine substituents. The two sides of the carbonyl group are then shielded by a bromine atom from one side and by a hydrogen atom on the other, rendering the bromine atoms ultimately more exposed to the metallated nucleophile.

4.1.2.5. **Synthesis of compound 124-Cl**

The unexpected result illustrated in the previous chapter led us to apply the same protocol using the chlorinated acetophenone 123-Cl. We did not expect that the carbonyl group of 123-Cl would be drastically more accessible than in 123-Br. In fact, the difference in atomic radius between chlorine and bromine is not large, and the crystal structure of the two compounds showed strong similarities. However, we expected that the lower reactivity of aryl chlorides in the metal-halogen exchange reaction might render the nucleophilic attack at the carbonyl a much more competitive process.

Indeed, exchanging the starting material from compound 123-Br to 123-Cl led to a different reaction outcome, and compound 124-Cl could be isolated. Nonetheless, the reaction protocol had to be slightly modified compared to the one reported in the previous chapter. Firstly compound 121 was lithiated by the addition of two equivalents of nBuLi at -78°C, and then the mixture was let warm up to room temperature. To the solution containing the in situ generated 127-Li, was then added 123-Cl and the

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*Fig. 109 Solid-state structure of compound 123-Br viewed from the vector passing through the carbon-oxygen bond parallel to the carbonyl plane.*

*Fig. 110 optimized procedure for the synthesis of 124-Cl*
mixture stirred for 15h at room temperature. After quenching the reaction mixture with water and washing the crude material with ethyl acetate, 124-Cl could be obtained with a yield of 54%.

The number of equivalents of "BuLi used in the reaction proved to be a crucial parameter for the obtainment of the product. The same reaction performed using only one equivalent of metalating agent delivered a crude mixture which contained compound 128 (Fig. 111) as the main component and, according to GC-MS analysis, no traces of the desired product. This outcome can be explained by taking into consideration the byproducts generated by the metalation with "BuLi. A stoichiometric amount of bromobutane is produced upon lithium-bromine exchange; if a second equivalent of "BuLi is present, a nucleophilic substitution reaction can take place, and octane and lithium bromide are generated. In the absence of a second equivalent of "BuLi, bromobutane remains in the reaction mixture. The two chlorine atoms of 123-Cl efficiently shield the carbon at the carbonyl group, and 127-Li reacts faster with the less hindered bromobutane via a nucleophilic substitution generating 128 (Fig. 111).

![Fig. 111 Reaction responsible for the generation of 128 when only one equivalent of "BuLi was used in the metallation of 121.](image)

4.1.2.6. Synthesis of compound 119-Cl

The connection of the donor moiety to the central carbon atom was completed via a Lewis-acid-catalyzed cyclization. In this reaction step, the first ring system of the future spiro center is created, and the central carbon atom reaches its final quaternary configuration. In the experimental procedure, excess boron trifluoride dimethyl etherate was added to a solution of 124-Cl in dry DCM under inert atmosphere. After aqueous workup and crystallization, compound 119-Cl was isolated in 62% yield. The reaction most likely proceeds via the generation of a trityl cation analogous promoted by the Lewis acid. The obtained cationic intermediate participates in an electrophilic aromatic substitution with one of the unsubstituted phenyl rings of the triarylamine fragment to yield the desired product.

![Fig. 112 Lewis-acid-catalyzed cyclization used for the creation of the spiro center in compound 119-Cl.](image)

The reaction could also be performed using a strong Brønsted acid and acetic acid as the solvent akin to what was reported by Adachi and coworkers in the synthesis of the analog 32. Employing these
conditions for the synthesis of 119-Cl resulted in a much lower yield of 26%, which brought us to prefer the Lewis acid promoted reaction.

4.1.2.7. Metalation of compound 119-Cl

![Metalation reaction scheme](image)

At this stage of the synthesis path, the conversion of 119-Cl to a bis organomagnesium- or organolithium-reagent (120-M) was investigated. Compared to aryl bromides, aryl chlorides display a lower reactivity in lithium-halogen exchange reactions and in the formation of Grignard reagents, which led us to choose particularly reactive metalating agent.309-310

![Metalating agents](image)

For the synthesis of 120-MgCl three different reagents were tested, the complex Mg(anthracene)-3THF and two particularly active kinds of magnesium powder, Rieke magnesium (MgR) and magnesium powder obtained from the decomposition of the complex Mg(anthracene)-3THF (MgA).310-312 Both magnesium powders are extremely finely dispersed and therefore highly reactive. As described by Bogdanović and co-workers, the decomposition of the Mg(anthracene)-3THF complex can be achieved either by thermal treatment in an inert solvent (i.e., toluene) or by removing the coordinated THF and the bound anthracene via sublimation under vacuum.311 For the generation of 120-Li, the lithiating agents 'butyllithium and lithium 4,4'-di-'butylbiphenylide (LiDBB) were tested. The conditions used for the generation and storage of LiDBB were akin to the one reported by the extensive study of Rychnovsky and co-workers.313

The metalation reaction was monitored by quenching aliquots of the reaction mixture with a proper reagent and then analyzing the product via NMR or GC-MS. A combination that was found particularly effective was the use of D2O as the quencher and the analysis of the mixture via GC-MS. Using a deuterated reactant coupled with mass spectroscopy enabled us to differentiate between the active metallated species and the ones quenched by other proton sources in the reaction mixture. At the same time, mixtures with several components could be easily analyzed thanks to the separation of the various
species via gas-chromatography. This procedure proved to be superior to NMR analysis, where signal superimposition complicated the analysis of complex mixture and did not deliver any information at all if excess of anthracene and 4,4'-di-tert-Butylbiphenyl were present.

In Fig. 115 is reported a typical series of GC chromatograms obtained during a reaction control where the samples were quenched with D$_2$O. The presented reaction monitoring corresponds to the reaction performed according to entry 4, Table 9. It can be clearly seen how the starting material is converted firstly to the mono-metallated species, which upon quenching generated compound 130, and subsequently to the bis metallated species, indicated by the detection of 129. Another species that could be detected in some metalation experiments is compound 131 which is most probably the product of the internal Ullmann-type coupling reaction between a metalated and a non-metalated chloro-functionality of compound 130.

![GC chromatograms](image)

*Fig. 115 Gas chromatograms obtained by the analysis of two reaction mixture samples quenched after 2 h and 16 h with D$_2$O. The metalation reaction was performed according to the condition of entry 4, Table 9.*

A summary of the most significant metalation experiments is reported in Table 9. The performed experiments show that except for Rieke magnesium, all the metalating agents employed reacted with compounds 119-Cl. A more detailed description of the reaction with LiDBB, Mg$^+$ and Mg(anthracene)-3THF is provided in the following sub-chapters. The tested reaction conditions did not cover all the possible combinations, and this screening should not be considered by any means an exhaustive study of the metalation of 119-Cl. In particular, the reactivity of 'BuLi was not further examined after the more convenient analysis via D$_2$O quench coupled with GC-MS was established.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>Stoichiometry</th>
<th>Temperature</th>
<th>Solvent</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>2</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>75°C</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>3</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>75°C</td>
<td>THF</td>
<td>Only partial metalation of the substrate was observed</td>
</tr>
<tr>
<td>4</td>
<td>Mg(anthracene)</td>
<td>Excess + EtO2</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>5</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>6</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>7</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>8</td>
<td>Mg(anthracene)</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>Increased amount of 131 is observed with respect to entry 6</td>
</tr>
<tr>
<td>9</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>-10°C</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>10</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>5°C</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>11</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>0°C</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>12</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>78°C</td>
<td>THF</td>
<td>Reaction quenched with BF3-OMe. NMR shows conversion to several products</td>
</tr>
<tr>
<td>13</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>78°C to RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
<tr>
<td>14</td>
<td>LiDBB, B(OiPr)3</td>
<td>Excess</td>
<td>RT</td>
<td>THF</td>
<td>No reaction</td>
</tr>
</tbody>
</table>

The metalation reaction was performed in presence of the boron electrophile. LiDBB reacts firstly with the boron reagent and no metalation was observed. The metalation reaction reached completion immediately after the addition of LiDBB is completed. Formation of compound 131 was observed. Reaction quenched with BF3-OMe. NMR shows conversion to several products. No reaction. Increased amount of 131 is observed with respect to entry 6. No reaction. Only partial metalation of the substrate was observed. No reaction.
4.1.2.7.1. Metalation using \( \text{Mg}^4 \)

The magnesium powder generated by the removal of anthracene and THF from the complex \( \text{Mg(anthracene)} \cdot 3\text{THF} \) under vacuum is a fine and highly pyrophoric powder. A large excess of this material was needed to achieve a complete metalation of \( 119-\text{Cl} \). In some experiments, only partial metalation of the substrate was observed even though the remaining \( \text{Mg}^4 \) still displayed a high reactivity and self-ignited in the presence of water. This outcome may suggest that the magnesium particles obtained via this method are highly hetero-dispersed and that only a small amount was reactive enough to achieve the metalation of both chloride functionalities. This aspect constitutes a quite significant drawback since, due to the large mass loss during sublimation, a rather large amount of the complex is needed to generate relatively small amounts of \( \text{Mg}^4 \). \( \text{Mg}^4 \) powder obtained by decomposition of the complex in toluene can also be used to achieve a complete metalation of \( 119-\text{Cl} \), but no experiments were performed to investigate whether stoichiometric amounts of the material would have been enough to convert the chlorinated starting material completely. Using excess \( \text{Mg}^4 \), it was possible to achieve double metalation of compound \( 119-\text{Cl} \) in THF, diethyl ether and MTBE; however, the solvent strongly influenced the reaction rate (entry 4, 5 and 6). At room temperature, in THF and MTBE the first metalation was relatively fast and reached completion after two hours. However, to achieve complete metalation of the second aryl chloride moiety, up to 16 h were needed. To accomplish a fast metalation in these two solvents, the reaction temperature had to be raised (entry 7). On the contrary, if diethyl ether was used as the reaction solvent, both aryl chloride moieties were fully metalated in two hours at room temperature.

In the experiments where THF was used as the reaction solvent, also the side product \( 131 \) could be detected. Its formation was rather slow at room temperature, but its generation rate was comparable to the metalations rate of the second chloride functionality. The similarity between the two reaction rates caused this compound to be a significant byproduct of the metalation reaction when THF was used.

4.1.2.7.2. Metalation using \( \text{Mg(anthracene)} \cdot 3\text{THF} \)

The reaction solvent also had a noticeable influence on the reaction outcome when the complex \( \text{Mg(anthracene)} \cdot 3\text{THF} \) was employed as the metalating agent. In THF, at room temperature, the magnesium complex is poorly soluble, and almost no conversion of compound \( 119-\text{Cl} \) could be detected after 24 h. If the temperature was raised, the solubility of the complex greatly increased together with its reactivity. However, using a stoichiometric amount of \( \text{Mg(anthracene)} \cdot 3\text{THF} \) only yielded the monometallated product. This outcome may be due to the fact that, at a temperature higher than r.t., the complex also reacts with THF, as reported by Bogdanović, which would reduce the amount of metalating agent available for the desired reaction.\(^{111}\) To achieve a complete metalation in this solvent, an excess of the complex may be therefore needed. The reaction temperature should also be optimized in a way that the losses due to reaction with THF are minimized, but at the same time, a sufficient solubility, and therefore a satisfying reaction rate, is obtained. The solubility of the \( \text{Mg(anthracene)} \cdot 3\text{THF} \) complex in MTBE appeared to be even lower than the one in THF. Upon dissolution of the bright orange complex, the solution normally acquired the same color; however, in the case of MTBE, the solvent remained colorless. Also, since MTBE cannot coordinate the magnesium atom as efficiently as THF, increasing the temperature did not result in an increase in the solubility of the reagent. At higher temperatures than r.t., the loss of one coordinated THF molecule was firstly observed (as evidenced by the change in color of the suspension from orange to yellow). Subsequently, the complex decomposed, generating anthracene and a finely dispersed magnesium powder. The in-situ generated magnesium powder afforded the complete metalation of \( 119-\text{Cl} \) in 4h at 75 °C using a stoichiometric amount of the complex.
4.1.2.7.3. Metalation with LiDBB

The metalation of 119-Cl with LiDBB in THF is extremely rapid, and by using an excess of the reagent, the metalation reaction reached completion in 1 h even at -95°C without the formation of by-products. However, by adding compound 119-Cl to a stoichiometric amount of the lithiating agent at 0°C also the undesired side product 131 was obtained (entry 12). Further experiments at lower temperature need to be performed to evaluate whether the generation of the by-product can be limited. However, in accordance with what reported later in chapter 4.1.2.7.4, we expected that lower temperature would not minimize the generation of 131 and that the stoichiometry employed had a much greater role in determining the product distribution. Generation of the reagent in MTBE and Et₂O was not possible, and therefore the reaction was not tested using the mentioned solvents. An open possibility that could still be tested is the use of binary mixtures of THF and another ethereal solvent.

4.1.2.7.4. Formation of compound 131

The formation of a side product could be recurringly observed in different metalation experiments (entries 4, 11, 13, Table 9). Based on the mass spectrometry and ¹H NMR data, we assumed that the detected species corresponded to compound 131 (Fig. 115). The formation of this side product was observed when either lithium- or magnesium-based reagents were employed. Its production also seemed to be linked to the use of THF as the solvent and to the presence of LiCl in the reaction mixture. We hypothesized that 131 might be generated by a Wurtz-like intermolecular coupling between a metallated and a non-metallated chloro-functionality of 119-Cl, as depicted in Fig. 116.

As previously described, the formation of compound 131 was highly competing with the metalation of the second chloride functionality if Mg⁴⁺ was used as the metalating agent and THF as the reaction solvent. In order to reduce the overall reaction time and favor the formation metalated product over compound 131, we attempted to combine the two metalating agents MgA and LiDBB in a tandem-metalation procedure (entry 14 Table 9). The first fast metalation was performed with Mg⁴⁺, and only traces of 131 were generated, whereas the second metalation was performed with the more reactive LiDBB. Even though the reaction could be indeed brought to completion much faster than using Mg⁴⁺ alone, the amount of 131 obtained was still considerable, suggesting that LiDBB may have an active role in its formation as well. However, the use of the same lithiating agent did not produce any byproduct when used in large excess and added very fast to a cooled solution of 119-Cl (entry 11, Table 9). Even though these last-mentioned reaction conditions avoided the formation of byproducts, they complicated the following reaction with the boron-based electrophile and the purification of the desired product. The excess of LiDBB could also react with the boron precursor, and the large amount of 4,4'-diterterbutylbiphenyl generated after workup could hamper the purification of the desired product.

![Fig. 116 Schematic representation of the reaction which supposedly leads to the formation of the side product 131.](image-url)
The coupling between an aryl halide and a Grignard reagent or between an aryl halide and an organolithium compounds are already known under the name of Kumada or Murahashi cross-coupling, respectively. However, this catalyzed reaction cannot be responsible for the generation of due to the lack of a transition metal species in the reaction mixture. The observed reactivity better matches the one reported by Hayashi and co-workers. In their works, they described the coupling between an aryl halide and an aryl Grignard reagent which proceeds without the use of any additional catalyst, relying on a radical-nucleophilic aromatic substitution mechanism (Fig. 117). As highlighted in their publication, the process is promoted by the presence of THF as well as LiDBB, which are in perfect agreement with the observations collected in our screening. The authors did not investigate the role of THF in the mechanism, but LiDBB was shown to be responsible for accelerating the initiation step where the radical anion of the aryl halide is generated. The effect of LiCl in promoting the formation of could be possibly attributed to the activating effect that the salt has on Grignard reagents. As postulated by Krasovskiy and Knochel, LiCl could help break the dimers that Grignard reagents often form, thereby rendering the metallated species more reactive. LiCl showed an activating effect also in some transition metal-catalyzed coupling where one of the reaction partners was a Grignard reagent.

![Fig. 117 Mechanism for the cross-coupling of aryl Grignard reagents with aryl iodides and bromides reported by Hayashi and co-workers.](image)

In our case, changing the reaction solvent proved to be sufficient to avoid the formation of 131. When either diethyl ether or MTBE were used no byproduct could be detected. Even though in MTBE the metatation reaction proceeds slower than in diethyl ether, this solvent was ultimately preferred because initial quenching experiments suggested that proton transfer from the solvent may occur when diethyl ether was employed. The synthesis towards 120-Li was not optimized since a metatation method was then already available, and possibly, the use of LiDBB is inevitably characterized by a competition between the metatation and the intermolecular coupling reactions. To achieve the twofold lithiation of compound 119-CI, the use of a different lithiating agent, i.e. 'BuLi, constitutes a more reasonable approach. The only attempt made to improve the outcome of the lithiation with LiDBB, was to perform the reaction in the presence of the boron electrophile to immediately trap the metataled species, thus avoiding the intermolecular coupling (entry 12, Table 9). Unfortunately, the reaction delivered as the main product the starting material 119-CI indicating that LiDBB reacts faster with the boron electrophile than with the chlorinated substrate.

4.1.2.8. Reactivity of 120-MgCl towards different boron-based electrophiles

This chapter analyzes the reactivity between 120-MgCl and different boron-based electrophiles for the introduction of the borylene bridge into the molecular backbone. In this synthesis step, the acceptor
fragment is completed, leading to the establishment of the spiro center and ultimately to the completion of the molecular scaffold. Different boron-based electrophiles were tested in the reaction by their direct addition to a solution containing 120-MgCl. For the screening presented in this chapter, the generation of 120-MgCl was performed under the condition reported in entry 7 (Table 9). The magnesium powder MgA generated by sublimation presented the advantage of being free from anthracene which simplified the reaction monitoring and the purification test of the obtained crude mixtures. The electrophiles used in this screening are reported in Fig. 118. The tested electrophiles were mainly reagents that would deliver products with a boron center that could be further functionalized in a following synthesis step. An exception was represented by Cl2{mesityl}B. The mesityl substituent cannot be easily replaced in the final product; however, using this reagent would allow the synthesis of a first stable derivative that could be used to test the properties of this class of compounds.

![Chemical structure](image)

*Fig. 118 Boron-based electrophiles tested in the reaction with 120-MgCl*

Trialkyl borates and the ether complexes of boron trifluoride are commonly employed electrophiles in the synthesis of organoboron compounds via the direct addition of an organometallic nucleophile. Aqueous workup was avoided in the experiment where either boron trifluoride dimethyl etherate, triisopropyl borate, or trimethyl borate were used. In these specific cases, we aimed to the isolation of an alkoxy or fluoride substituted product that would allow a more direct functionalization via the addition of another nucleophile. Instead, an acidic aqueous workup was performed in the reactions where diisopropylamino borane was employed, which yielded the borinic acid 37-OH as the reaction product.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF3·OMe2</td>
<td>Complex mixture with possibly traces of the product.</td>
</tr>
<tr>
<td>2</td>
<td>B(OPr)3</td>
<td>37-OPr could be detected</td>
</tr>
<tr>
<td>3</td>
<td>B(OMe)3</td>
<td>37-OMe could be detected</td>
</tr>
<tr>
<td>4</td>
<td>H2B=N(Pr)2</td>
<td>37-OH could be detected</td>
</tr>
<tr>
<td>5</td>
<td>Cl2BMes</td>
<td>No product could be detected</td>
</tr>
</tbody>
</table>

*Table 10 List of the different boron electrophiles tested in the reaction with 120-MgCl and the outcomes of the different experiments.*
As summarized in Table 10, the result of the brief screening showed that when BF<sub>3</sub>·OMe<sub>2</sub> was used, complex crude mixtures were obtained. NMR analyses suggested that the obtained crude material may have contained traces of the desired product; however, purifications of the obtained mixtures were unsuccessful. The reaction with Cl<sub>2</sub>(mesityl)B yielded a less complicated reaction mixture but NMR and GC-MS analysis did not suggest that the desired product was contained in the crude mixture. In contrast, generation of the desired product could be observed when triisopropyl borate, trimethyl borate, and diisopropylamino borane were used (entries 2, 3, and 4). According to the NMR spectra of the crude material, the desired product was the main species present in the mixture. In Fig. 119 and Fig. 120, spectrum 1 correspond the NMR spectra of the crude mixture relative to entry 3 and 4, respectively. To better show the signal belonging to the reaction product, the spectra of the crude are compared to the corresponding purified materials (spectrum 2).

![Fig. 119 Section of the ¹H NMR spectra of the crude material generated by the procedure of entry 2 (spectrum 1), compared to the ¹H NMR spectrum of pure compound 37-OPr (spectrum 2). The solvent signal is marked with the symbol *](image-url)
Fig. 120 Section of the $^1$H NMR spectra of the crude material generated by the procedure of entry 4 (spectrum 1), compared to the $^1$H NMR spectrum of pure compound 37-OH (spectrum 2).

In conclusion, triisopropyl borate, trimethyl borate, and diisopropylamino borane showed to be suitable electrophiles for the installation of the borylene bridge into the molecular backbone. In contrast, the use of boron trifluoride dimethyl etherate or the functionalized Cl$_2$(Mesityl)B did not produce promising results. Since the use of the two electrophiles B(OMe)$_3$ and B(OPr)$_3$ would give access to two analogous compounds with comparable reactivity, we decided to focus our attention on the synthesis of compound 37-OPr. We supposed that the isopropoxide substituted product should be slightly less prone to hydrolysis, and we expected that this property would be beneficial during the purification steps. The description of the purification and the strategies employed for the derivatization of these two compounds are reported in detail in chapter 4.1.5. One important observation that could be made during this screening was that the metatation performed with Mg$^A$ was not always reproducible. Specifically, different amounts of Mg$^A$ were needed to reach complete metatation depending on the batch of the magnesium powder. This observation had to be added to the already mentioned drawbacks relative to this reagent, namely, the need for an excess of the metatating agent and the low atom economy related to its generation. The lack of reproducibility cause also the generation of crude mixtures with different qualities, which posed an additional challenge in the search for a reliable purification method for compound 37-OPr.

4.1.2.8.1. Synthesis of 37-OH with Mg(anthracene)-3THF

An efficient and robust purification method for crude mixtures containing 37-OH was developed during the exploration of the synthetic paths reported in chapter 4.1.3. This procedure allowed to isolate the desired product despite the presence of a large number of impurities. For instance, the presence of a large amount of anthracene did not hinder the isolation of 37-OH, and, for this reason, the choice of the metatating agent in the synthesis of 37-OH was not necessarily restricted to Mg$^A$. Therefore, we attempted the synthesis of the borinic acid using Mg(anthracene)-3THF and MTBE as the reaction solvent.
The Grignard reagent \textbf{120-MgCl} was generated according to entry 4 (Table 9), and subsequently, diisopropylamino borane was added to the reaction mixture. As already reported in chapter 4.1.2.7.2, Mg(anthracene)∙3THF decomposes under these conditions, generating Mg\(^{\text{A}}\) in situ and releasing a stoichiometric amount of anthracene. This reaction procedure presented three main advantages compared to one that used isolated Mg\(^{\text{A}}\) generated via sublimation. The magnesium complex could be used in a stoichiometric amount, increasing the atom efficiency of the metalation reaction. The in-situ generated magnesium powder did not need to be isolated, reducing the risks of quenching the reagent. Lastly, the Grignard reagents could be obtained in a reproducible fashion. The use of MTBE in this reaction is fundamental. As mentioned in chapter 4.1.2.7.2, the low solubility of the magnesium complex in this solvent and the solvent's low-coordinating ability were the key factors that allowed the in-situ generation of Mg\(^{\text{A}}\). An additional advantage of using this solvent is that the generation of the Grignard reagent \textbf{120-MgCl} can be achieved without the generation of the side product \textbf{131}.

![Reaction scheme depicting the synthesis of compound 37-OH using Mg(anthracene)-3THF in MTBE.](image)

Fig. 121 Reaction scheme depicting the synthesis of compound 37-OH using Mg(anthracene)-3THF in MTBE.

Indeed, following this procedure, compound \textbf{37-OH} could be synthesized; purification of the crude material according to the procedure discussed in chapter 4.1.5.2.1 delivered the desired product with a yield of 44%.

4.1.2.9. Summary

The synthesis approach explored in this chapter proved to be a suitable strategy for the construction of the targeted molecular scaffold. An unfortunate combination of the reactivity and the steric bulk of the bromine substituents in compound \textbf{123-Br} did not allow the synthesis of the initially targeted intermediate \textbf{119-Br}. Fortunately, the analog compound \textbf{119-Cl} proved to be accessible and allowed the continuation of the synthesis path. Careful optimization of the reaction between \textbf{119-Cl} and particularly reactive magnesium reagents led to the generation of a two-times metalated intermediate \textbf{120-M}. The so-obtained Grignard reagent could be successfully reacted with three different boron-based electrophiles giving access to three members of the targeted compound class. The purification and derivatization of compounds \textbf{37-OH} and \textbf{37-O\text{Pr}} is treated in chapter 4.1.5; a comparison between this synthesis path and the other two alternatives treated in this thesis is discussed in chapter 4.1.6.
4.1.3. Introduction of the borylene bridge at the beginning of the synthesis sequence.

4.1.3.1. Introduction

Parallel to the synthesis route reported in the previous chapter, we investigated a complementary synthesis path which is summarized in Fig. 122. In this alternative synthesis sequence, the boron atom is introduced in the first stages of the synthesis route, and only afterward the molecular scaffold is completed.

![Diagram of synthesis sequence](image)

*Fig. 122 Schematic representation of the synthesis sequence discussed in this chapter where the borylene bridge is inserted at the beginning of the synthesis path.*

Concerning the method used for the introduction of the boron center, we decided to rely on the procedure previously reported by Cheung and Miao for the synthesis of derivative 134-OH (chapter 4.1.1.1, Fig. 90). The reported procedure involves the combination of a doubly metallated intermediate with a boron-based electrophile, in analogy to what had been described in chapter 4.1.2. Alternatively, the introduction of the boron atom could have been performed via a silicon/tin-boron exchange reaction. More specifically, either the synthesis procedure reported by Piers and co-workers, or Yamaguchi and co-workers could be used to obtain either compound 134-Cl or 134-Br, respectively (chapter 4.1.1.2). To all effects, this second strategy implies the inclusion of an additional step in the synthesis path compared to the one where the metalated intermediate is combined directly with a boron-based electrophile. Moreover, these procedures do not offer a marked advantage with respect to the procedure of Cheung and Miao since the generation of a metallated intermediate is nonetheless needed for the synthesis of the organosilicon or organotin derivatives. Considering the above-mentioned points we decided to ignore these alternative possibilities.

The borylated starting material 134-R was then subjected to further transformations to complete the construction of the molecular scaffold. Firstly, compound 134-R was oxidized to the ketone 135-R taking care that the bonds between the boron center and the aromatic rings were not compromised. Subsequently, the synthesis path could be completed by applying the same two-steps sequence described
in the synthesis of 32 or in chapter 4.1.2. Namely, the addition of a metallated triphenylamine and the acid-catalyzed cyclization. These two last steps are analogous to the steps reported in the previous chapter; however, the reaction conditions needed to be adapted compatibly to the presence of the boron atom.

The choice of the substituent R was also crucial, and it was made considering mainly three aspects. The substituent had to be compatible with the reaction condition employed, it should possibly help protect the boron atom from unwanted cleavage, and it must allow the derivatization of the boron center once the molecular backbone was completed. In the following sub-chapters, the different synthesis steps are commented on in detail.

4.1.3.2. **Synthesis of compound 134-OH and 134-DMEA**

Borinic acids are easily accessible compounds that, like boronic acids, are stable under atmospheric conditions and relatively versatile as far as derivatization of the hydroxy group is concerned. For these reasons, we first choose to synthesize the borinic acid 134-OH as the borylated starting material of the synthesis path. As already mentioned in chapter 4.1.1.1, Cheung and Miao already reported a synthesis procedure for this compound. In their procedure, the authors reacted a twofold lithiated substrate with trisopropyl borate and successfully obtained compound 134-OH in 84% yield after aqueous workup. The introduction of the borylene bridge is performed by taking advantage of the same kind of reaction used in chapter 4.1.2, but in this pathway, it does not represent a major synthesis challenge. Compound 133 is much more easily accessible than compound 119-X, and the procedure used for its synthesis does not pose any limitation on the kind of halogen atoms that can be present in its structure. Therefore, in contrast to what had been observed with compound 124-X, the generation of the nucleophile via metalation did not require an extensive experimental effort for the optimization of the reaction conditions.

A straightforward and commonly performed derivatization of the boron center is the reaction with a chelating ligand that could form an internal Lewis acid-based adduct. For this kind of derivatization, different ethanolamine or hydroxyquinoline derivatives have been employed. In our case, we opted for the synthesis of compound 134-DMEA (Fig. 123). With the synthesis of this compound, we wanted to verify if the ethanolamine ligand can act as a removable protecting group for the boron center by providing a temporary reduction of its Lewis acidity. Additionally, the internal Lewis acid-base formation could provide additional steric bulk, thus rendering nucleophilic attacks at the heteroatom less likely.

![Fig. 123 Synthesized derivatives of 134-R. 134-OH is characterized by a tricoordinated boron atom, whereas the boron center in 134-DMEA is tetracoordinated.](image)

The synthesis of compound 134-OH was not performed via the published procedure but by adapting the protocol developed by Pucheault et al., in analogy to the reaction described in chapter 4.1.1.7.1. The procedure involves the formation of the Grignard reagents in situ, under Barbier conditions, in the
presence of diisopropylamino borane as the boron source. After acidic workup and purification with column chromatography compound 134-\( \text{OH} \) was obtained in 67\% yield.

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{N= BH}_2 & \quad \text{133} \\
\text{134-} \text{OH} & \quad \text{134-} \text{OH}
\end{align*}
\]

**Fig. 124** Reaction procedure used for the synthesis of compound 134-\( \text{OH} \).

This procedure is quite convenient from a practical point of view with respect to the previously published method. The major advantages are that the reaction is performed in only one step without the need for an extra lithiation step and using simple magnesium turnings as the metalating agent. However, the obtained yield is inferior to the one of the published example. The inferior result may be depending on the different reaction conditions or eventually from the employed purification method, which was not reported for the synthesis procedure of Cheung and Miao.

The synthesis of compound 134-\( \text{DMEA} \) was achieved by simple addition of a stoichiometric amount of dimethylethanolamine to a methanol solution of 134-\( \text{OH} \). The desired product was obtained in 57\% yield, calculated from compound 133.

4.1.3.3. **Synthesis of compound 135-\( \text{OH} \)**

\[
\begin{align*}
\text{64-R} & \quad \text{Oxidant} \\
\text{65-R} & \quad \text{R = -OH, -O-}
\end{align*}
\]

**Fig. 125** The second stage of the synthesis pathway consisted of the oxidation of the methylene fragment of 134-R.

Compound 135-R constituted a more challenging target compound than its precursor since a similar oxidation reaction in the presence of a borinic acid functionality has not been reported in the literature. In the published examples that are more closely related to this transformation, the starting material for the oxidation are triarylboranes, and in all the cases, the boron atom is protected, either by means of steric bulk or rigid planarization of the structure.\(^{289, 324}\) In compound 134-R, the boron center is more exposed when compared to the published examples and, as reported by Brown and Dodson, a decrease in the steric bulk around the boron atom in triarylboranes renders the B-C bonds more susceptible to oxidation.\(^{325}\)

The oxidation conditions that had been screened are summarized in Table 11. The tested oxidizing agents were \( \text{CrO}_3 \), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and \( \text{O}_2 \) in combination with \( \text{tBuOK} \) and 18-crown-6. The oxidation with chromium-based reagents has been used for the introduction of a carboxylic group in the above-mentioned protected triaryl borane, but no indications whether this method was compatible with a borinic acid fragment were available. DDQ was used for the oxidation of similar moieties but in compounds with other heteroatoms instead of boron (i.e. silicon, oxygen or sulfur).\(^{326}\) The \( \text{tBuOK} \)-promoted oxidation with molecular oxygen published by Wang et al. proved to be
Successful in the oxidation of a wide range of molecules at the benzylic positions but has not been applied in the oxidation of organoboron compounds. Nonetheless, we decided to include the procedure in our screening due to its extreme simplicity and the fact that it did not generate reaction byproducts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Reagent</th>
<th>Solvent</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>134-DMEA</td>
<td>DDQ</td>
<td>MeOH</td>
<td>Oxidation of the amine ligand</td>
</tr>
<tr>
<td>2</td>
<td>134-DMEA</td>
<td>CrO₃</td>
<td>CH₃COOH</td>
<td>Oxidation of the amine ligand</td>
</tr>
<tr>
<td>4</td>
<td>134-OH</td>
<td>DDQ</td>
<td>MeOH</td>
<td>Product detected</td>
</tr>
<tr>
<td>5</td>
<td>134-OH</td>
<td>O₂, tBuOK, 18-crown-6</td>
<td>DMF</td>
<td>Product detected</td>
</tr>
</tbody>
</table>

Table 11 Screened reaction condition for the oxidation of compounds 134-OH and 134-DMEA.

Initially, compound 134-DMEA was used as the substrate for the reaction (Entry 1 and 2) since we assumed that a tetracoordinated boron center might be more stable and protected than the free borinic acid 134-OH. Compound 134-DMEA was reacted with both an inorganic (CrO₃) and an organic oxidizing agent (DDQ). In both experiments, the signal detected in the $^{11}$B NMR spectra of the crude mixtures was drastically shifted compared to the one observed for the starting material. Specifically, the signals shifted from 7.6 ppm to 29.2 ppm and 40.5 ppm in the oxidations conducted with CrO₃ and DDQ, respectively. This significant shift probably indicates that the dimethylethanolamine chelating substituent reacted with the oxidizing agent and was detached from the boron center. Moreover, the shift of 29.3 ppm detected in the reaction with CrO₃ would suggest that the detected species is not a boric or a borinic acid ester but rather a boronic acid ester obtained by the oxidation of one B-C bond of the starting material. As a consequence of the above-mentioned findings, in the following screenings experiments, CrO₃ was excluded. Since the coordination of the amine did not offer any protective effect, the free borinic acid 134-OH was used as the substrate. DDQ was again tested as the oxidizing agent together with the combination of O₂, tBuOK and 18-crown-6 (Entry 5). In both cases, the product could be detected, but the conditions of entry 4 delivered a crude NMR with minor traces of byproducts in contrast to the one obtained with the conditions of entry 5. Moreover, the reaction conducted with DDQ reached completion in 2 h, whereas for the O₂ promoted oxidation, complete conversion was obtained after 2 days. The byproducts present in the crude material of entry 5 were not characterized, which hampered the quantification of the relative amount of product contained in the mixture. To allow a qualitative comparison of the two outcomes, the NMR spectra of the two mixtures are reported in Fig. 126.
The main side product of the oxidation reaction with DDQ is the corresponding reduced hydroxyquinone which is generated in stoichiometric amounts. Crystallization with different solvents or solvent mixtures proved to be ineffective in the selective removal of this byproduct. Another strategy often employed for the purification of small borinic acids is the formation of their ethanolamine adducts as compound \(134-\text{DMEA}\). These compounds usually display a much lower solubility compared to their related borinic acids and can be therefore easily washed or crystallized. For this reason, the crude mixture of entry 4 was also treated with ethanolamine, and crystallization was again attempted, but, unfortunately, also this procedure did not lead to the pure reaction product.

Purification of the crude material was then attempted via column chromatography. A successful separation was achieved using a tertiary mixture composed of dichloromethane, methanol, and triethylamine. Triethylamine was initially incorporated in the mixture to reduce the acidity of the stationary phase and facilitate the elution of the borinic acid, which would otherwise strongly interact with the silica gel. Unexpectedly, the combination between the organic base and the borinic acid produced the opposite effect. In the presence of triethylamine, compound \(135-\text{OH}\) eluted even slower on the column. This finding could still be used to our advantage in the purification of compound \(135-\text{OH}\). A small percentage of triethylamine was kept in the eluent mixture until all the by-products had been completely eluted. Its percentage was then slowly decreased while the methanol component was increased to ensure the elution of the desired product.

Fig. 126 Section of \(^1\)H NMR spectrum of the crude material obtained applying the conditions of entry 4 (spectrum 1) and entry 5 (spectrum 2). In spectrum 2, the observed prominent signals belong all to the desired product \(135-\text{OH}\). The solvent signal is marked with the symbol \(*\).
Using the above-illustrated oxidation and purification protocols, compound 135-OH was synthesized in 48% yield. Since no major by-products could be seen in the NMR spectra of the crude mixture, we assumed that the relatively unusual and relatively long chromatographic procedure together with the intrinsically high affinity of borinic acids for silica gel may account for the loss of material. After this procedure was established, Yamaguchi and co-workers reported the oxidation of the double benzylic position of a triaryl borane under nearly identical conditions. Their procedure, however, delivered the desired product with a yield of 87%. Even though the reaction procedure was almost identical to the one adopted for our substrate, the employed conditions for the chromatographic separation were remarkably different due to the different interactions that triarylboranes and borinic acids have with silica gel. This observation would support the hypothesis that the purification step was responsible for the mediocre yield of the reaction.

A possible way to improve the outcome of this reaction could be the use of the potassium difluoro borate derivative 135-F₂K as starting material. As reported by Ham and co-workers, benzyl alcohols with an aryl trifluoroborate functionality can be oxidized to the corresponding ketones using the Jones reagents without compromising the boron center. The use of 135-F₂K as an adduct for the oxidation reaction could improve the purification procedure since these salts usually display high crystallinity and are normally purified via simple crystallization.

An alternative synthesis route towards compound 135-OH that was also considered but never applied is reported in Fig. 128.

The starting material of the synthesis sequence is compound 123-Br which preparation had already been discussed in chapter 4.1.2.3. In this synthesis path the problematic related to the compatibility between the oxidation reaction and the boron atom is removed. The carbonyl group is, in fact, present in
the molecular structure since the beginning of the sequence, and it is protected by the formation of a 1,3-dioxolane. Deprotection of the carbonyl group at the end of the sequence should then yield the desired compound 135-OH. The viability of the proposed synthesis pathway is supported by reported works in which the same strategy was applied for the introduction of a boronic acid ester fragment via lithiation and addition of a suitable boron-based electrophile.329

This alternative synthesis and the use of potassium fluoroborate in the oxidation reaction were not investigated. The established oxidation protocol furnished enough material for the progression of the synthetic path, and the completion of the synthesis sequence was prioritized against its optimization.

4.1.3.4. Synthesis of compound 136-R and completion of the molecular scaffold

In analogy with the synthesis sequences already discussed in chapters 4.1.2.4 and 4.1.2.5, the following step of the synthesis path consisted in connecting the donating triarylamine fragment to the molecular structure. The employed synthesis strategy was equivalent to the one illustrated in the previous chapters and implied the addition of a metallated triarylamine 127-M to the carbonyl group of the ketone 135-R (Fig. 129). Different variations of the two reactants were tested to find the best combination of reagents that would ensure a successful nucleophilic addition at the carbonyl group without involving the boron center.

![General reaction scheme for the synthesis of compound 136-R](image)

The ketones used in this small screening were compounds 135-OH, 135-OHQ and 135-OB. Whereas, as reaction partners, both the Grignard reagent 127-MgBr and the lithiated compound 127-Li were tested. The use of the less reactive magnesium reagent was considered despite the negative results obtained in chapter 4.1.2.4 and 4.1.2.5 since we expected the mentioned carbonyl compounds to show a greater reactivity compared to the one displayed by 123-Cl and 123-Br. Due to the introduction of the borylene bridge in the molecular framework, we expected the molecular structure to be planar and the carbon atom of the carboxyl group to be more accessible. These assumptions were supported by the reported solid-state structure for compound 134-OH and by the solid-state structure of 135-OHQ obtained in the context of this work. In Fig. 130 it can be clearly seen that the additional link provided by the borylene...
bridge impedes the rotation of the two aromatic rings and produces a more rigid and planar molecular structure with a carbonyl group that is not shielded by other atoms.

Fig. 130 OTEP drawings of the solid-state structure of compound 135-OHQ.

The boron atoms in the borinic acid 135-OH and its anhydride are tricoordinated and therefore constitute a potential competing site for a nucleophilic attack. For this reason, also compound 135-OHQ was tested in the reaction. In the hydroxyquinoline derivative, the interaction between the nitrogen lone pair and the empty p orbital of the boron center leads to the formation of a stable tetracoordinated chelated complex. We expected that the formation of this adduct would lower the Lewis acidity of the boron and provide additional steric shielding around the atom, thereby favoring the attack at the carbonyl group and improving the reaction outcome. The hydroxyquinoline derivative 135-OHQ was synthesized by the simple addition of 8-hydroxyquinoline to the borinic acid in THF. The obtained material displayed a marked green-yellow fluorescence once irradiated with UV light. This characteristic is a common photophysical property of many compounds containing a borylated hydroxyquinoline fragment and is not particularly relevant in the context of this work. However, this characteristic luminescence might be used as a visual probe to verify the integrity of the tetracoordinated boron center as the reaction proceeded. Compound 135-OB was synthesized from compound 135-OH via thermal dehydration under reduced pressure.

The reaction between the Grignard reagent 127-MgBr and 135-OB or 135-OHQ led to no conversion even upon an increase of the reaction temperature. In contrast, the lithiated triarylamine 127-Li reacted with all the three substrates producing different outcomes (Table 12). During the screening process, it was observed that the in-situ generation of 127-Li negatively influenced the reaction reproducibility and complicated the execution of experiments on a small scale. We, therefore, decided to generate and isolate the lithiated amine 127-Li. The compound was synthesized by adding nBuLi to a solution of the brominated starting material 121 in diethyl ether instead of THF. The low solubility of the product in the ethereal solvent caused its precipitation. Filtration of the obtained solid led to the isolation of the diethyl ether complex of compound 127-Li with a yield of 55%. Using the isolated material, a freshly prepared solution of the lithiated triarylamine with a precise concentration could be generated precisely by weight, and additional source of error as the presence of unreacted nBuLi or quenching the stock solution upon storage could be ruled out.

The crude reaction mixtures obtained using 135-OH and 135-OHQ as starting materials (Entry 3 and 4) contained a large amount of triphenylamine together with small amounts of boron-based starting materials.
material as well as a small amount of a new product. Also in this case, increasing the reaction temperature did not modify the outcome of the reaction. Additionally, it must be noted that upon addition of the lithiated amine to 135-OHQ (entry 3), the characteristic luminescence of this compound completely disappeared. These outcomes would possibly indicate that compound 127-Li interacted with the boron atom of the two starting materials forming a borate salt that was then hydrolyzed during the workup procedure. However, this behavior would be particularly unexpected for compound 135-OHQ since the tetracoordinated boron atoms should be less susceptible to nucleophilic attacks. In the crude of these two reactions was also possible to detect the signals associated with the ring closed product 37-OH indicating that, for some extent, the spontaneous ring closure of the second ring system at the spiro center was also occurring.

The reaction between 127-Li and 135-OB (entry 5) delivered a completely different result, no traces of triphenylamine or of starting material could be observed. Instead, only the same new signals already observed in entry 4 could be detected, which further supported the hypothesis that the signal may belong to the desired product 136-R. Purifications of the three crude mixtures obtained in entry 3, 4 and 5 was attempted using column chromatography. For entry 4 and 5 silica gel was used as the stationary phase whereas for entry 5 C18 reverse phase silica was employed. In all cases the purification processes did not lead to the isolation of the tertiary alcohol intermediate 136-R. However, some column fractions containing compound 37-OH were isolated. This unexpected outcome validated the hypothesis of spontaneous formation of the spiro center, possibly, not only during the reaction but also during the chromatographic separation. These results also showed that the complexation with hydroxyquinoline did not protect the boron center during the reaction or the chromatographic separation, which defeated the advantage of using this ligand as a protecting group.

<table>
<thead>
<tr>
<th>Entry</th>
<th>M</th>
<th>Boron precursor</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg</td>
<td>HQ</td>
<td>No reaction</td>
</tr>
<tr>
<td>2</td>
<td>Mg</td>
<td>OB</td>
<td>No reaction</td>
</tr>
<tr>
<td>3</td>
<td>Li</td>
<td>HQ</td>
<td>Poor conversion</td>
</tr>
<tr>
<td>4</td>
<td>Li</td>
<td>OH</td>
<td>Poor conversion</td>
</tr>
<tr>
<td>5</td>
<td>Li</td>
<td>OB</td>
<td>Complete conversion</td>
</tr>
</tbody>
</table>

*Table 12 Screened reaction conditions for the synthesis of compound 136-R.*

Since the preliminary attempts to purify compound 136-R delivered poor results, its isolation and characterization were not further investigated. Instead, we analyzed the direct synthesis of the final spiro compound by the adoption of a one-pot procedure (Fig. 131). The reaction conditions of entry 5 (Table 12) were combined, without performing any intermediate treatment, with a second cyclization step to form compound 37-OH directly. The obtainment of the desired compound would then support the hypothesis that the new compound observed in the previously described reactions indeed corresponded to 136-R.
**Fig. 131 Alternative one-pot procedure, designed to overcome the impossibility of isolating compound 135-OB.**

Firstly, we investigated if the cyclization reaction could be brought to completion by using a dehydrating agent without the need for a Lewis or Brønsted acid. As previously mentioned, the failed attempt of isolating the tertiary alcohol intermediate via column chromatographic yielded small amounts of the final product 37-OH. We, therefore, speculated that a spontaneous cyclization of 136-OH could take place if the reaction equilibrium were pushed towards the product by eliminating the generated water from the reaction mixture. To test this hypothesis, the crude mixture, obtained from the addition of 127-Li to 135-OH was subjected to aqueous workup, the crude material dissolved in CDCl₃ and molecular sieves were added. The reaction was then monitored via NMR spectroscopy. Unfortunately, the obtained NMR spectra did not show clean conversion to one product but rather a complex mixture. Due to the discouraging results, this approach was not further analyzed. However, it is possible that using a different reaction solvent, i.e. benzene or toluene, may positively influence the reaction outcome.

We then proceeded in testing a Lewis and a Brønsted acid in the cyclization reaction namely, BF₃·OEt₂ and HCl. From our experience with this transformation reported in 4.1.2.6, as well as from the results reported by Adachi and co-workers, we forecasted that performing the reaction with Brønsted acids in aqueous media would yield poor results. We, therefore, decided to perform also the reaction involving HCl under anhydrous conditions by using a solution of HCl in dry cyclopentyl methyl ether (CPME). The reaction substrate for both tests was the crude material generated by following the conditions reported in entry 5 (Table 12). The obtained material was not subjected to an aqueous workup; instead, the reaction solvent was evaporated and replaced with the one needed in the following step. We were, in fact, also interested in evaluating whether the reaction could be condensed in a truly one-pot procedure without the need for an intermediate workup stage. The cyclization reaction promoted with BF₃·OEt₂ was performed in benzene, whereas the reaction that was performed with HCl in CPME was performed using dioxane as the solvent.

Using either BF₃·OEt₂ or the anhydrous solution of HCl, the desired compound 37-OH could be detected in the crude mixtures. From a quantitative evaluation of the obtained NMR spectra, the amount of the desired compound accounted for about 40% of the reaction mixture in both cases. These positive results showed that isolation of the intermediate tertiary alcohol 136-R was unnecessary and that combining the two reactions in a single one-pot procedure could effectively yield the desired product.
applying the purification reported later in chapter 4.1.5.2.1, compound **37-OH** could be isolated with a yield of 30% starting from compound **135-OB**.

4.1.3.5. **Summary**

The synthesis strategy explored in this chapter could be successfully applied to the synthesis of compound **37-OH** and therefore constitutes an alternative pathway to the one developed in chapter 4.1.2. The early introduction of the boron atom in the molecular structure strongly influenced the choice of the reaction conditions and posed some challenges in the synthesis and purification of some intermediates. The third ligand “R” at the boron atom plays an important role in determining the reaction outcome, as it could be especially observed in chapters 4.1.3.3 and 4.1.3.4. Although a brief optimization of these two reaction steps was performed, testing other compounds with different ligands at the boron center may improve the reaction yield and or the crude mixture purification of the above-mentioned synthesis steps. A comparison between this synthesis strategy and the other paths developed in this work is provided later in chapter 4.1.6.
4.1.4. Introduction of the borylene bridge via boron-tin or boron-silicon exchange at the end of the synthetic sequence

4.1.4.1. The exchange reaction applied to the synthesis of 37-R

This section discusses the synthesis of compound 37-X (X = Cl, Br or I) via tin- or silicon-boron exchange. When projecting this synthesis path, we decided to adapt the examples discussed in chapter 4.1.1.2 (Fig. 101) to our molecular scaffold. In these reported procedures, a dimethyl(diaryl)silane or -stannane was used as the starting materials, which led us to target compounds 137-Si and 137-Sn as precursors, respectively (Fig. 132). The synthesis of the two compounds will be presented separately in the following paragraphs. As reaction partners, only trihaloboranes were employed, and the reaction between the silicon and tin precursors with alkyl or aryl dihaloboranes was not investigated. We expected that the lower reactivity of the substituted haloborane compared to the unsubstituted boron halides would hinder the substitution reaction with compound 137-Si. Moreover, this approach would imply the separate synthesis of different and dedicated reactants. Therefore, we found that a more flexible approach would be achieved if the exchange of the substituent at the boron center was performed after the exchange reaction.

![Fig. 132 Targeted silicon and tin precursors for the the synthesis of compound 37-X via silicon- or tin-boron exchange reaction.](image)

Compounds 138-Si and 138-Sn (Fig. 134) could eventually be used as alternative substrates. These alternative starting materials could be particularly useful if methylation of the boron center or halogenation of the silicon or tin atom hindered the second exchange reaction, as observed in the synthesis of compounds 102 and 107 (Fig. 97, chapter). Using these alternative substrates, the transformation could then be described as the intermolecular version of the exchange reaction reported by Haubold and co-workers (Fig. 133). The reaction could then proceed via two subsequent silicon/tin-boron exchange reactions and the elimination of two molecules of bromotrimethylsilane or -stannane. Alternatively, the insertion of the boron atom could also proceed via two different tin/silicon-boron exchanges followed by the elimination of BX3, in analogy to the synthesis of compound 107 (Fig. 97).

![Fig. 133 Synthesis of bromodiphenyrborane via silicon-boron exchange.](image)

However, the synthesis route needed to obtain compounds 138-Si and 138-Sn may render the use of these substrates not particularly advantageous. The silicon or tin functionalities cannot be inserted at the beginning of the synthesis path by synthesizing a silylated or stannylated ketone, analogous to compound 123-X. In analogy to what had been reported in chapter 4.1.2, the two silicon- or tin-based fragments
would introduce even more steric bulk around the carbonyl group than the one observed in compound 123-X. As a consequence, the subsequent nucleophilic attack at the carbonyl group would be even more hampered, rendering the synthesis route not applicable. On the other hand, the introduction of the silicon or tin center via the reaction between the metallated substrate 120-M and two equivalents a proper silicon or tin electrophile would still need to rely on the difficult metalation of compound 119-Cl. This pathway could therefore constitute a valid alternative only if the subsequent exchange reaction brings a considerable improvement compared to the direct reaction with the boron electrophile reported in chapter 4.1.2.8.

For the reasons mentioned above, we decided to examine only the synthesis and subsequent exchange reaction of compounds 137-Si and 137-Sn.

Fig. 134 Alternative substrates for the synthesis of 37-X via the silicon- or tin- boron exchange reaction.
4.1.4.2. Introduction of the borylene bridge via boron-silicon exchange

The synthesis path towards the silicon precursor 137-Si had been designed in analogy to the route discussed in chapter 4.1.3, and it is reported in Fig. 135. The introduction of the silicon center is performed in the first stage of the synthesis pathway by the reaction between a double metalated nucleophile and dimethyldichlorosilane. The obtained compound is then oxidized, and formation of the spiro center is achieved via the synthesis of the tertiary alcohol 141 and its subsequent cyclization. This reaction sequence takes advantage of the stability of the organosilicon moiety, which can be installed at the beginning of the synthetic path and does not get compromised during the oxidation of the double benzylic position or the nucleophilic attack at the carbonyl functionality. These assumptions are based on the fact that a method for synthesizing compound 140 had been previously reported, and the compound itself has even been used in reactions that involved the attack of martalated species at its carbonyl group. In addition, we expected compound 140 to have a relatively planar molecular geometry in analogy to what had been observed for compound 135-R. Therefore, we were confident in the fact that the reaction with the metallated amine 127-Li would not present in the same problem encountered for compounds 123-Cl and 123-Br and that the silicon center would not be compromised. We forecasted, however, that the ring closure step from compound 141 to compound 137-Si may need to be optimized due to the tendency of the carbon-silicon bond in organosilanes to be cleaved in the presence of fluoride ions or strong acids.

The synthesis of compound 140 could be achieved following the reported experimental procedures. For this reason, the synthesis path will be discussed starting from the addition of the metallated amine 127-Li to compound 140.

Fig. 135 Reaction sequence employed for the synthesis of the silicon precursor 137-Si.
The synthesis of compound 141 was performed by adding a THF solution of compound 140 dropwise to a THF solution of freshly produced 127-Li cooled to -78°C. After 30 minutes, the reaction was warmed up to room temperature, and an aqueous workup was performed. The NMR spectra obtained by analyzing the crude mixture via $^1$H NMR spectroscopy presented broad signals which were hardly interpretable. The analysis of the crude via mass spectrometry, however, indicated that the analyzed mixture was composed mainly of two compounds, namely, 141 and 137-Si. This analysis suggested that spontaneous cyclization to compound 137-Si may have occurred during the reaction. Two distinct fractions could be isolated via column chromatography, one containing pure compound 137-Si and one containing, according to mass spectrometry measurements, the mixture of the two compounds 141 and 137-Si. This results further confirmed that compound 141 could spontaneously convert to compound 137-Si. Also, the NMR spectra of the isolated binary mixture evolved with time and conversion from what we assume to be compound 141 to 137-Si was observed. Fig. 136 illustrates the evolution with time of the $^1$H NMR spectra of the mixed fraction obtained from column chromatography. Immediately after separation, the $^1$H NMR spectra presented broad signals which were hard to interpret (spectra 1). After 20 minutes at room temperature, the signals became slightly less broad, and their relative intensities dramatically changed (spectra 2). The final set of signals largely matched the one corresponding to the pure 137-Si (spectra 3).

![Fig. 136 $^1$H NMR spectra showing the spontaneous conversion of compound 141 to compound 137-Si. Spectrum 1 corresponds to the $^1$H NMR spectrum of the isolated mixed fraction, measured directly after the separation was performed. Spectrum 2 corresponds to the $^1$H NMR spectrum of the same sample measured after storing the NMR tube for 20 minutes at room temperature. Spectrum 3 corresponds to the $^1$H NMR spectrum of the isolated pure fraction containing only compound 137-Si. The increase in the amount of compound 137-Si is clearly indicated by the increase in signal intensity of the peaks marked with the symbol *. The solvent signal, when recognisable, is marked with the symbol †.](image)

On a preparative scale, conversion of compound 141 to compound 137-Si was achieved by dissolving the mixture of the two compounds in chloroform and stirring the solution overnight in the presence of molecular sieves. Following this procedure, compound 137-Si was obtained in 58% yield from compound
An additional confirmation that the desired compound was obtained was delivered by its solid-state structure, obtained by analyzing single crystals of the compound via X-ray diffraction (Fig. 137).

4.1.4.2.2. **Boron-silicon exchange experiments**

The boron-silicon exchange experiments conducted using compound **137-Si** as the substrate are summarized in Table 13. In this screening, three boron trihalides had been tested, namely, **BCl**₃, **BBr**₃, and **BI**₃. The reactions were performed in NMR tubes which were flame-sealed after all the reagents were mixed. In the case of **BBr**₃, the borylation experiments were conducted both in solution and in neat conditions. By conducting the borylation experiment in solution, it was possible to regularly monitor the reaction via NMR, which allowed us to investigate the influence of temperature on the reaction progress in one single experiment. In contrast, the reactions conducted in neat conditions needed to be interrupted and processed before they could be analyzed. The workup of the reactions was performed by removing the excess of boron trihalide under vacuum and dissolving the residue in deuterated chloroform. The obtained solution was then analyzed by means of NMR spectroscopy. The boron trihalide reagent was always used in excess with respect to compound **137-Si** except for one experiment conducted with **BI**₃ (Table 13, entry 9).

![Fig. 137 ORTEPs of the solid-state structure of compound 137-Si.](image1)

![Fig. 138 Schematic representation of the boron-silicon exchange reaction from compound 137-Si to compound 37-X.](image2)
<table>
<thead>
<tr>
<th>Entry</th>
<th>Boron trihalide</th>
<th>Temperature</th>
<th>Reaction time</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BCl₃</td>
<td>From r.t. to 95 °C</td>
<td>16 h at r.t., 1 h at 95°C</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>2</td>
<td>BBr₃</td>
<td>r.t.</td>
<td>1 h</td>
<td>Neat</td>
</tr>
<tr>
<td>3</td>
<td>BBr₃</td>
<td>100 °C</td>
<td>36 h</td>
<td>Neat</td>
</tr>
<tr>
<td>4</td>
<td>BBr₃</td>
<td>100 °C</td>
<td>6 h</td>
<td>Neat</td>
</tr>
<tr>
<td>5</td>
<td>BBr₃</td>
<td>120 °C</td>
<td>2 d</td>
<td>Neat</td>
</tr>
<tr>
<td>6</td>
<td>BBr₃</td>
<td>100 °C</td>
<td>20 min</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>7</td>
<td>BBr₃</td>
<td>From r.t. to 95°C</td>
<td>14 h at r.t., 16 h at 100°C</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>8</td>
<td>BBr₃</td>
<td>From r.t. to 120°C</td>
<td>20 h at r.t., 15 h at 60°C, 2.5 d at 100°C, 4 d at 120°C</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>9</td>
<td>BI₃</td>
<td>From r.t. to 120 °C</td>
<td>5 d at r.t., 3 h at 100°C,</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>10</td>
<td>BI₃ᵇ</td>
<td>From r.t. to 120 °C</td>
<td>4 d at r.t., 3 h at 120°C,</td>
<td>CDCl₃</td>
</tr>
</tbody>
</table>

Table 13 Summary of the performed silicon-boron exchange experiments for the synthesis of compound 37-X using 137-Si as the silylated precursor. a sample was initially briefly and gently heated up with the heat gun to ensure dissolution, b BI₃ was used in a stoichiometric amount.

4.1.4.2.2.1. Exchange reaction with BCl₃

Only one reaction was performed using BCl₃ as the borylating agent (entry 1). In the experiment, a solution of the boron trihalide in n-hexane was added to a DCM solution of compound 137-Si at room temperature. The NMR monitoring of the reaction revealed that no reaction occurred under these conditions or even upon heating the reaction mixture up to 95°C for more than 24h. Therefore, the reactivity of BCl₃ was considered insufficient to perform the examined silicon-boron exchange and further experiments were not conducted.

4.1.4.2.2.2. Exchange reaction with BBr₃

The experiments with BBr₃ were conducted in CDCl₃ solutions or in neat BBr₃, and the tested temperature span from r.t. to 120°C (entry 2 to 7). As expected, the more Lewis-acidic boron electrophile displayed a different reactivity compared to the one of BCl₃. New signals in the ¹H NMR spectra could be detected already at room temperature a few minutes after the addition of BBr₃. To interpret the outcome of the NMR analysis, all the different possible reaction pathways were considered (Fig. 139).
scheme, the crossed pathways correspond to the reactions that should be disfavored according to the reactivity reported in the literature.

![Diagram of possible transformations](image)

**Fig. 139** Schematic summary of the possible transformations that can originate from the reaction between 137-Si and BBr3.

The spectra recorded for entry 8 are reported in Fig. 140 and largely resemble the one obtained for the other experiments. The signal at 0.63 ppm assigned to the methyl groups attached to the silicon center was highly recognizable and was therefore used to monitor the conversion of the starting material and the formation of new products. We expected that the first and second exchange and eventual methyl-transfer reactions would generate different brominated methyl silanes, which would, in turn, give rise to new signals in the aliphatic region of the spectra. For the discussion and interpretation of the results, several NMR reference data for different silanes had been collected from the literature and summarized in Table 27 in the Appendix section.

The different experiments showed that, at room temperature, the starting material takes approximately 2 days to be completely consumed and a shorter time when the sample is heated. In all the experiments performed in solution, two new peaks in the region between 0.9 and 0.65 ppm could be detected at the beginning of the reaction, while the singlet of the starting material slowly disappeared.
As the reaction proceeded, the intensity of the three signals diminished, and simultaneously two prominent signals accompanied by two minor ones started increasing in the region between 0 and 0.35 ppm. Lastly, the prominent central signal at around 0.5 ppm decreased while the two other signals increased, and no other changes were then detected. The same trend was also observed in the neat experiments, which were interrupted at different times. Due to the kind of workup performed, we could also conclude that the newly observed signals belong to non-volatile species that were not easily removed under vacuum.

Both reaction pathways that would lead to compound 37-Br include a first exchange reaction that generates compound 142 and SiMe$_2$Br. Subsequently, compound 142 can undergo an intramolecular exchange reaction yielding the desired product 37-Br together with SiMe$_2$Br$_2$. Alternatively, compound 37-Br can be generated from compound 142 in a two-steps sequence. It is possible, in fact, for another intermolecular boron-silicon exchange to take place yielding compound 143 and SiMe$_2$Br$_2$, followed by an intermolecular cyclization and elimination of BBr$_3$. Independently from the path followed by the reaction, SiMe$_2$Br$_2$ (boiling point 112.3°C) and SiMe$_3$Br (boiling point 79.5°C) should be produced, and we expected the first byproduct to be detectable at least in the solution experiments due to its relatively high boiling point. Unfortunately, none of the signals observed in the aliphatic region matched with the reference values for SiMe$_2$Br$_2$ or for SiMeBr$_3$, that could be generated by the reaction between of SiMe$_2$Br$_2$ and BBr$_3$. The signals also did not correspond to the reported values for BMeBr$_2$ (Table 27, appendix), which would be generated in the event of a methyl transfer. The presence of BBr$_3$ in the solution may have a big influence on the signals’ shift; however, the same peaks were also detected in the neat
experiments where excess BBr₃ and other volatile components were removed. Therefore, in the spectra of the neat experiments, we would not expect an influence of BBr₃ on the shift of the NMR signals, and we would also expect a difference in the relative intensity of the peaks in the aliphatic region. The treatment under reduced pressure should, in fact, partially deplete or completely remove SiMe₂Br and SiMe₂Br₂.

New NMR signals were not only detected in the aliphatic region but also in the aromatic portion of the NMR spectra. In conjunction with the appearance of the signals between 0.35 and 0 ppm, new signals with a doublet structure at 8.2 ppm could be detected. A similar behavior was observed for other boron-silicon exchange reactions between BBr₃ and molecules containing the 9,10-dihydro-9,9-dimethyl-9-silaanthracene fragment. In both cases, the signal with the highest shift in the ¹H NMR spectra of the reagent and product has a doublet multiplicity, and it is found at higher ppm in spectra of the reaction product. The same effect can also be observed by comparing the NMR spectra of compounds 139 and 134-OH in which the doublet signal found at the highest ppm has a shift of 7.61 ppm and 7.97 ppm, respectively. This behavior strongly indicates that this effect is indeed produced by the substitution of the silicon with the boron atom. We hypothesize that this doublet is associated with the protons in ortho position with respect to the silicon atom since these atoms are likely to be highly influenced by the exchange reaction. New signals in the aromatic region at even higher ppm are detected when the sample was heated at 120 °C; however, their emergence was not coupled with the appearance of new clear signals in the aliphatic region. Instead, the existing signals broaden and start to show a sort of multiplicity. Additionally, the aromatic region itself becomes rather complex and characterized by many signals. As can be deduced from this description, the observation gathered by the analysis of the ¹H NMR spectra was insufficient to deliver a complete picture of the reaction and confirm the generation of the desired compound.

The analysis of the ¹³C NMR spectra, unfortunately, did not furnish more information about the reaction outcome. The aromatic region of the carbon spectra was relatively crowded, which rendered the reaction monitoring using this data a complex task. Additionally, the signals of the carbon atoms directly attached to the boron center are difficult to detect. The signal of the carbon atom in ortho position with respect to the one attached to the silicon atom does not generally undergo a diagnostic shift in the exchange reaction as reported for the protons. Additionally, for Me₂SiBr₂, no reliable reference for its ¹³C spectra could be found in the literature. Also, the comparison between the data reported for other halogenated organosilanes and the signals’ shift in the measured ¹³C NMR spectra would point towards the formation of a multiply halogenated silicon atom bound to an aromatic system.

The analysis via ¹¹B NMR spectroscopy revealed a much simpler picture since only one prominent broad peak at around 54 ppm was detected in all the experiments. Only in reactions at high temperature, after an extended reaction time, two sharper peaks at around 58 and 63 ppm could be detected. As reported in Table 14, the shift of the ¹¹B NMR signal for diaryl(bromo)boranes is distributed over a relatively wide interval and varies depending on the molecular structure. The acceptor fragment of 37-Br structurally corresponds to 9-bromo-9,10-dihydro-9-boraanthracene, which shows a shift of 58 ppm for its ¹¹B NMR signal (Table 14) and is reasonably closer to the one detected in the silicon-boron exchange experiments. It must be noted, however, that the shift of the ¹¹B NMR signal for aryl(dibromo)boranes covers a range that significantly overlaps with the one of diaryl(bromo)boranes (Table 14). Therefore, with the analysis of the ¹¹B NMR spectra, we could not confirm the generation of compound 37-Br; however,
the observed shift would suggest that at least one boron-silicon exchange took place and that at least compound 142 was generated.

In many reported procedures, where the exchange reaction is performed in neat BBr₃, the desired products readily precipitate from the reaction mixture. Colorless crystals suitable for X-ray diffraction analysis indeed precipitated from the reaction mixture of entry 3. To our surprise, the solid-state structure obtained from the X-ray diffraction analysis of the crystals did not correspond to the one of the desired products but to the one of compound 147 (Fig. 141). The isolated compound is a salt with a tetrabromoborate anion, and a cationic partner derived from compound 137-Si. The cationic nature of the fragment derives from the protonation of the nitrogen atom of the triarylamine moiety, whereas the silicon atom is brominated and attached to only one of the two aromatic rings. In the ¹¹B NMR spectrum of the crystal, a major signal at 39 ppm and a minor signal at 26 ppm were detected, possibly indicating the hydrolysis of the tetrabromoborate anion which should display a signal at much lower ppm. The comparison between the ¹H NMR of the crystals and the one obtained in entry 3 showed a strong correspondence suggesting that the main component of the mixture for this entry was possibly compound 147. In all the other experiments, the ¹H NMR spectra also contained these signals but not as a main component. It is also worth noting that a doublet at 8.20 ppm is observed in the aromatic region of the ¹H NMR spectrum of the isolated crystal. This observation is important since it indicates that the detection of signals in this area is also connected to the bromination of the silicon atom and not only by its substitution with boron. Unfortunately, it was not possible to unambiguously assign a signal of the ¹H NMR of the crystal to the methyl group attached to the silicon atom due to different signals present in the aliphatic region. The obtainment of compound 147 can be explained by the accidental presence of traces of moisture in the reaction mixture that could hydrolyze BBr₃ and lead to the generation of HBr. The acid would then lead to the cleavage of the Si-C bond and the halogenation of the silicon atom as well as to the protonation of the triarylamine moiety. Two other reactions could theoretically cause the production of HBr in the reaction mixture. Namely ring closure reaction of brominated aryl silane speculated by Kaufman and Gross (Fig. 98) or the borylation of an unsubstituted aryl moiety with BBr₃ observed by Wagner and co-workers. Both reactions are, however, not likely to occur under the conditions and with the substrates of the above-mentioned experiments. Additionally, no evidence for the formation of their reaction products could be collected.

![Solid state structure and molecular scheme of compound 147.](image)

**Fig. 141 Solid state structure and molecular scheme of compound 147.**
### Bromodiaryl boranes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{11}$B NMR shift (solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structure 1]</td>
<td>72.1 ppm ($C_6D_6$) $^{335}$</td>
</tr>
<tr>
<td>![Structure 2]</td>
<td>66.4 ppm ($C_6D_6$) $^{336}$</td>
</tr>
<tr>
<td>![Structure 3]</td>
<td>58 ppm ($CDCl_3$) $^{337}$</td>
</tr>
<tr>
<td>![Structure 4]</td>
<td>41.8 ppm ($C_6D_6$) $^{338}$</td>
</tr>
</tbody>
</table>

### Dibromoaryl boranes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{11}$B NMR shift (solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Structure 5]</td>
<td>61.7 ppm ($C_6D_6$) $^{339}$</td>
</tr>
<tr>
<td>![Structure 6]</td>
<td>56.2 ppm ($CDCl_3$) $^{340}$</td>
</tr>
<tr>
<td>![Structure 7]</td>
<td>56.2 ppm ($CDCl_3$) $^{341}$</td>
</tr>
<tr>
<td>![Structure 8]</td>
<td>55.9 ppm ($CDCl_3$) $^{342}$</td>
</tr>
</tbody>
</table>

Table 14 $^{11}$B NMR reference of some selected bromo and dibromo arylboranes.

In the effort to gather more details on the outcome of the exchange reaction, the crude mixture of entry 6 was quenched with mesityllithium. Unfortunately, in the obtained material, no traces of $^{37}$-Mes could be detected. With the data collected in this screening we could state that compound $^{137}$-Si reacts with BBr$_3$ either in solution or in neat condition generating, between different species, a borylated product. However, no evidence that this route could lead to the desired compound $^{37}$-Br were obtained, and for this reason, no further experiment had been performed.

#### 4.1.4.2.2.3. Exchange reaction with BI$_3$

The experiments conducted with BI$_3$ (entry 8 and 9) were performed only in solution; however, reactions in neat boron triiodide are theoretically possible thanks to the relatively low melting point of the reagent of 49.9 °C. Despite its high commercial cost, BI$_3$ can be synthesized on a multigram scale via the reaction between sodium borohydride and iodine which are relatively inexpensive reagents. Therefore, the use of the reagent in large excess or the eventual upscaling of the reaction scale was not considered unpractical. The outcome and the general course of the reactions were comparable to what was observed in the reactions with BBr$_3$. The main difference was that some of the detected signals were shifted towards higher ppm and that the reaction proceeded much faster. The conversion of the starting material also appeared to proceed in a much more defined way.
In the performed experiments, new signals in the aliphatic and aromatic region of the $^1$H NMR spectrum were already detected at room temperature a short time after the addition of B$_3$I$_3$. A signal at 0.73 ppm was detected simultaneously with three other signals at lower ppm, at 0.49, 0.29, and 0.20 ppm. In analogy to the reaction with BBr$_3$, the intensity of the signal at 0.73 ppm decreased with time until disappearance while the signal at 0.29 initially increased. The two peaks at 0.49 and 0.20 kept increasing their intensity as the reaction proceeded, while the peak at 0.29 ppm slowly vanished. In the aromatic region, two new signals at 8.24 ppm and 8.06 ppm with a doublet multiplicity were detected. As observed in the reactions with BBr$_3$, the shift of these new signals was higher than the one of the starting material. One of the most significant differences between these experiments and the reactions performed with BBr$_3$ is that even after heating the mixture at 120 °C for three hours, no additional signals at even higher ppm than 8.24 were observed. Instead, new signals, at around 8.11 ppm were detected.

Initially, in the $^{11}$B NMR spectra, only one new prominent broad peak at around 43 ppm was detected. With the proceeding of the reaction, two sharp peaks at 18.36 and 36.27 ppm could also be observed. The comparison with the values reported in the literature, which are less abundant for this class of compounds (Table 15), did not help to furnish a univocal indication on which products were present in the solution. However, the relatively low shift of the broad peak observed in the $^{11}$B NMR spectra would suggest the obtainment of an aryl diodoborane derivative.
An experiment with a stoichiometric amount of BI$_3$ was also performed to investigate the influence of the amount of borylating agent on the outcome of the reaction (Entry 9). In this experiment, equal amounts of silicon precursor 137-Si and BI$_3$ were let react together, applying the same conditions used for the experiments with excess BI$_3$. From the $^{11}$B NMR spectrum, it was possible to monitor the disappearance of BI$_3$, which signal at -8.1 ppm did not only decrease but also broadened and shift to lower ppm. The sharp peak at 18 ppm was also observed again, with the broad prominent peak around 43 ppm. Both peaks increased their intensities with the progress of the reaction.

Generally, the use of BI$_3$ produced cleaner crude mixtures than the ones with BBr$_3$. However, the similar behavior of the reactions did not suggest that the outcome was drastically different from the one observed with boron tribromide; therefore, further investigations with this reagent were not performed.

### 4.1.4.3. Introduction of the borylene bridge via boron-tin exchange

The introduction of the boron center via boron-tin exchange was also briefly explored. Our main interest was to evaluate whether using the more reactive tin precursor 137-Sn in the transmetalation reaction would generate a different outcome than what had been observed for 137-Si. We expected that the use of a more reactive, tin-based starting material should offer an advantage in the less favored exchange reactions. As previously illustrated in chapter 4.1.4.2, the second exchange event from compound 142 to either 37-Br or 143 is a crucial step for the obtainment of the desired product. However, it may be hampered by partial halogenation of the silicon atom and methylation of the boron atom. Therefore, we forecasted that the use of 137-Sn should facilitate this reaction step and be beneficial to obtain the desired product.

For the synthesis of the tin precursor 137-Sn, an analogous synthesis sequence to the one adopted for 137-Si could have been possibly employed. However, no tin analogous of compound 140 had been previously reported. Due to the lower stability of organostannanes compared to their analogous organosilanes, we feared that the synthetic pathway used for the preparation of 137-Si may not be suitable for the synthesis of compound 137-Sn and that a careful and time-consuming adaptation of the synthetic sequence may be required. Given the explorative nature of this screening, we decided to take advantage of the synthesis protocol developed in chapter 4.1.2 and install the dimethyl-tin moiety at the last stage of the reaction path, as indicated in Fig. 143.
To obtain compound \textbf{137-Sn}, \textit{Cl}_2\text{SnMe}_2 was reacted with the doubly metalated \textbf{120-MgCl} which generation had been discussed before. It is worth noting that the synthesis of compound \textbf{137-Sn} was performed before the metalation reaction towards \textbf{120-MgCl} had been optimized. For this reason, the generation of the Grignard reagent was performed in THF using Mg\textsuperscript{A} as the metalating reagent, which led to the presence of the side product \textbf{131} in the reaction mixture (see chapter 4.1.2.7). Also, the magnesium dust, used in the synthesis of \textbf{137-Sn}, was generated from the complex Mg\{anthracene\}\cdot3THF by sublimation. An intrinsic limitation of this process was that anthracene traces could still be present in the final magnesium powder and, therefore, in the final crude product. Due to the similar retention time, \textbf{137-Sn} and anthracene could not be separated via column chromatography, and even purification via crystallization failed in delivering the pure product. Due to the challenging purification and the low reproducibility in the metalation reaction with Mg\textsuperscript{A} it was not possible to obtain an analytically pure sample of compound \textbf{137-Sn}. Nonetheless, two small samples were anyway tested in the reaction with both BCl\textsubscript{3} and BBr\textsubscript{3}. We considered the presence of anthracene or compound \textbf{131} to be acceptable since the two compounds should not react with BCl\textsubscript{3} and only under particularly harsh conditions with BBr\textsubscript{3}.

In methystannanes, the \textit{\textsuperscript{1}H} NMR signals associated with the methyl groups show a characteristic multiplicity which was also observed in the case of compound \textbf{137-Sn}. As shown in Fig. 144, the signal is constituted by a central singlet and two satellites characterized by a doublet multiplicity and a lower intensity (accounting for about 6\% of the main signal). These less intense satellites are generated by the coupling between the proton nuclei and the nuclei of the two tin isotopes \textit{\textsuperscript{117}Sn} and \textit{\textsuperscript{119}Sn}. The central signal is instead generated by the protons bonded to the non NMR active Sn atoms. Measuring the distance between the inner peaks of the satellites yields the \textit{\textsuperscript{117}Sn-H} coupling constant, whereas the distance between the outer peaks of the satellites corresponds to the \textit{\textsuperscript{119}Sn-H} coupling constant. For compound \textbf{137-Sn} the measurements delivered the values of 55.7 Hz and 58.4 Hz for \textit{\textsuperscript{117}Sn-H} and \textit{\textsuperscript{119}Sn-H}, respectively, which are in line with the one observed for compounds \textbf{148} and \textbf{149} (Fig. 144).

The isotope \textit{\textsuperscript{115}Sn} is also NMR active but its lower natural abundance and lower gyromagnetic ratio translate into a lower natural receptivity. For instance, its receptivity relative to \textit{\textsuperscript{1}H} (1.24\cdot10\textsuperscript{-4}) is one order of magnitude lower than the one of \textit{\textsuperscript{117}Sn} (3.49\cdot10\textsuperscript{-3}) and \textit{\textsuperscript{119}Sn} (4.51\cdot10\textsuperscript{-3}). As a consequence, this isotope generates much weaker signals which are normally not detected.
The described coupling constants are influenced by the substituents that are present at the tin center together with the methyl groups. For instance, fluorination of the backbone in compound 99 generated a slight increase of the $^{117/119}$Sn-H coupling constants when compared to the hydrogenated compound 149 (Fig. 144). A more drastic change of the coupling constant values is observed when methyl stannanes with a different number of halogen atoms at the tin center are compared. As reported in Table 28, in the Appendix section, the observed $^{2}J$ $^{117/119}$Sn-H can increase up to 20 Hz after a methyl group is substituted with a halide. The measurement of the $^{117/119}$Sn-H coupling constants of the signal associated with the methyl group is therefore a useful tool for monitoring tin-boron exchange reactions. These values can be used to evaluate the number of halogen atoms present at the tin center and therefore obtain more information about reaction progress and generated intermediates. As reported by Petrosyan and Roberts, an additional advantage of these parameters is that, unlike the shift of the associated signal, the coupling constants are not affected by the solvent employed in the NMR measurement. We, therefore, expected that monitoring the aliphatic region of compound 137-Sn would deliver more information than what could be obtained in the case of its silicon analog. An extensive list of $^{117/119}$Sn-H coupling constants for some methyl stannanes is reported in Table 28 in the Appendix section.

Fig. 144 Left, section of the $^1$H-NMR spectra of compound 137-Sn in C$_6$D$_6$ highlighting the signal assigned to the methyl groups and the measured values for the $^{117/119}$Sn-H coupling constants of the same signal. Right, comparison between the same $^{117/119}$Sn-H coupling constants of some reported compounds. 283, 288, 343
Table 16 summarizes the most significant reaction parameters of the two conducted tin-boron exchange experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Boron trihalide</th>
<th>Temperature</th>
<th>Reaction time</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>BCl&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>From -78°C to r.t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1 day</td>
<td>CDCl&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>BBr&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
<td>From r.t to 75°C&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2 days</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;D&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> the sample of 137-Sn utilized in the reaction contained anthracene impurities that could not be separated. <sup>b</sup> A sub-stoichiometric amount of BCl<sub>3</sub> (1M in hexane) is used, <sup>c</sup> the addition was performed at -78 °C and then let reaction mixture react at room temperature, <sup>d</sup> the sample of 137-Sn utilized in the reaction contained also compound 131 that could not be separated, <sup>e</sup> Excess of neat BBr<sub>3</sub> is used, <sup>f</sup> the sample was heated at 70 °C for 1h and at 75 °C for 2h

In the reaction conducted with BCl<sub>3</sub> (entry 1), a stoichiometric amount of the boron trihalide was used. In the NMR measurement that followed the addition of the boron trihalide, no peak for free BCl<sub>3</sub> could be observed in the <sup>11</sup>B NMR spectrum, suggesting that the boron trichloride completely reacted. At the same time, the peak at 17 ppm indicated that most probably also hydrolysis took place since this shift is close to the one associated with boronic acids. In the <sup>1</sup>H NMR spectra measured in this experiment, the appearance of signals at higher ppm in the aromatic region was detected. As already mentioned in the previous chapter, these new signals could be connected to the introduction of a more electron-withdrawing substituent on the aromatic system, which can either be achieved by borylation of the aromatic ring or halogenation of the tin center. During the reaction, the methyl signal of compound 137-Sn vanished and one new signal at 0.03 ppm with a <sup>2</sup>J<sup>119</sup>Sn-<sup>1</sup>H of 62.25 Hz was observed. Comparing the change in the coupling constant with the trend observed in the reported data suggested that the methyl signal belongs to a species with one chlorine atom at the tin center. The shift associated with the signal is much lower than the one of other compounds with one chlorine atom bonded to the tin atom, such as Me<sub>3</sub>SnCl or Me<sub>2</sub>SnPhCl. However, a signal in this region was also observed for compound 147.
Fig. 145 NMR spectra recorded during the reaction monitoring of entry 1 (Table 16). Spectrum 1, starting material before the addition of BCl₃. Spectrum 2, reaction mixture after the addition of BCl₃. Spectrum 3, Me₂SnCl₂ is added to the reaction mixture. The signals marked with ✭ correspond to anthracene. The signal marked with ✬ could be assigned to Me₂SnCl₂. The solvent signal is marked with the symbol ⋄.

The analysis of the collected data would suggest that a first boron-tin exchange took place and that the generated product successively underwent hydrolysis. Additionally, in the NMR spectra, a small signal with one visible satellite was detected at 1.20 ppm which could be assigned to Me₂SnCl₂ (Fig. 145, signal marked with ✬). This observation could suggest that the complete boron-tin exchange could possibly take place under these conditions if the hydrolysis reaction is avoided.

In the reaction with BBr₃, a large excess of the boron trihalide was used, and the reaction followed a similar course to the one observed for the silicon-based compound 137-Si. In the aromatic region of the ¹H spectra, new signals at higher ppm were detected. In particular, the signal at 8.64 ppm, was clearly composed of many overlapping peaks. In the aliphatic region, a peak at 0.93 ppm was initially observed, which then disappeared during the reaction and 6 new signals appeared in the region between 0.3 and 0.65 ppm (Fig. 146).
Fig. 146 $^1$H NMR spectra recorded during the reaction monitoring of entry 2 (Table 16). Spectrum 1, reaction mixture analyzed before the addition of BBr$_3$. Spectrum 2, reaction mixture analyzed directly after the addition of BBr$_3$. Spectrum 3, reaction mixture analyzed after keeping the sample for 16 h at room temperature. Spectrum 4, reaction mixture analyzed after heating the sample at 70°C for 1 h. Spectrum 5 reaction mixture analyzed after heating the sample at 75°C for 2 h. The signals marked with $\star$ belong to compound 131. The solvent signal is marked with the symbol $\star$.

The quality of the spectra allowed us to identify the satellites and measure the coupling constants only for the peak at 0.93 ppm. The obtained value for $^2J\text{ }^{119}\text{Sn}-^1\text{H}$ was 66.08 Hz which could correspond with the one published for Me$_2$SnBr$_2$. No references in the same solvent are available in the literature; however, as previously mentioned, the coupling constants do not vary considerably when the solvent is changed. The detection of Me$_2$SnBr$_2$ should be connected to the generation of the desired product 37-Br.

The only discrepancy with this interpretation is that the signals at higher ppm in the aromatic region, possibly associated with a borylation reaction, appear only later when the other alkyl signals can be observed. Unfortunately, the quality of the signals did not make it possible to measure the coupling constants for these new peaks, and the lack of references did not allow any further comparison.

Together with the signal assigned to BBr$_3$ in the $^{11}$B NMR spectrum, two new peaks could be observed at 27.8 and 62.9 ppm. The signal at 27.8 ppm could be assigned to impurities of hydrolyzed BBr$_3$ contained in the reagent utilized, whereas the signal at 62.9 may indicate the formation of the desired product (Table 14). As already mentioned in chapter 4.1.4.2.2, the shift of the $^{11}$B signal alone cannot provide a confirmation of the obtainment of the desired product.

These preliminary results did not exclude that this route could lead to the desired product; however, due to time restraints and the limited amount of 137-Sn that could be synthesized, no further experiments were conducted.
4.1.4.4. Summary

In this chapter, the silicon/tin-boron exchange reaction was applied to the two substrates $^{137}$Si and $^{137}$Sn in the effort to synthesize compound $^{37}$X. A robust and straightforward synthesis towards compound $^{137}$Si could be quickly established thanks to the presence of a reported procedure for the synthesis of compound $^{140}$. The precursor for the silicon-boron exchange reaction, $^{137}$Si, was therefore easily accessible in a pure form, allowing a first broad screening of the reaction conditions. In contrast, the synthesis of compound $^{137}$Sn was based on the not-optimized version of the metalation described in chapter 4.1.2.7 and carried the downsides characterizing that reaction step. Additionally, compound $^{137}$Sn proved to be difficult to obtain in a pure form if two byproducts of the metalation reaction, anthracene and-or compound $^{131}$, were present in the reaction mixture. Due to these limitations, only two experiments involving the use of compound $^{137}$Sn could be performed.

The performed silicon and tin boron exchange reactions did not lead to a conclusive answer on whether these methods would be suitable for the synthesis of compound $^{37}$X. To better understand the outcome of the reaction, further experiments under different conditions must be performed and the species generated during the reaction characterized. Additionally, to justify further investigation on the tin-boron exchange reaction, an alternative synthesis route to compound $^{137}$Sn should be found since the same synthesis method can be used to insert the boron atom in the molecular structure directly. In contrast, if the silicon-boron exchange reaction successfully delivered the desired product, this synthesis route would constitute a valid alternative to the reaction path explored in chapter 4.1.3. The presence of the silicon atom in the molecular scaffold eases the generation purification of the oxidized intermediate $^{140}$ in comparison to the methods employed for compound $^{135}$-R. Also, the addition of the metallated triarylamine to the carbonyl group concatenated to the ring closure step requires a less elaborated procedure. It is, however necessary to develop a reliable and practical silicon-boron exchange procedure to conclude the reaction path and verify its superiority.
4.1.5. Purification and reactivity of the spiro compounds 37-OPr and 37-OH

The synthesis sequences established in chapter 4.1.2 and 4.1.3 gave access to two compounds 37-OPr and 37-OH. In this chapter, their purification and different strategies for their derivatization are discussed.

4.1.5.1. Compound 37-OPr

4.1.5.1.1. Purification

The isopropoxy derivative 37-OPr was synthesized using the method reported in chapter 4.1.2.8. The synthesis sequence consisted in the double metalation of 119-Cl with MgA, which generated the Grignard reagent 120-MgCl. The metallated species was then reacted with B(OPr)3, delivering 37-OPr. An aqueous workup was excluded to avoid the cleavage of the isopropoxy substituent from the boron center, which implied that the magnesium salts generated during the reaction were included in the generated byproducts. The purification methods that guarantee the exclusion of moisture, thus completely excluding the risk of hydrolysis, are crystallization, selective extraction with proper solvents, and sublimation. Normal phase column chromatography was excluded since the acidic nature of the silica gel would lead to the hydrolysis of the alkoxy substituent. Column chromatography could have been applied by using a reverse-phase stationary phase and choosing a suitable eluting mixture and elution method, e.g. incorporating isopropanol in the mobile phase and using a relatively fast chromatographic method.

Good results in terms of purity of the obtained product were achieved by extracting the reaction crude material with a DCM-Hexane mixture and subsequently washing the obtained solid with toluene. Following this procedure, the desired product 37-OPr was obtained in 40% yield starting from compound 119-Cl. Evaporation of the toluene solution revealed that a significant amount of product was still dissolved in the solvent; therefore, optimizing this last stage should improve the reaction yield. Other tested purification methods included extraction of the material with acetonitrile or crystallization from DCM by the slow addition of hexane, but those procedures delivered worse results. The crystallization from DCM yielded single crystals which were analyzed via X-ray diffraction, which revealed that the isolated material corresponded to the hydrolyzed compound 37-OH. Purification by means of sublimation was not attempted.

As already mentioned in chapter 4.1.2.7.1, due to the difference in the quality of the various MgA batches, problems with the reproducibility of the metalation reaction were encountered. This factor caused variations in the amount and relative distribution of byproducts and impurities (e.g. anthracene) in the crude mixtures. Therefore, establishing a standard procedure that reliably delivered the compound with a reasonable purity proved challenging. Applying the above-mentioned extraction and crystallization procedure led only one time to an isolated material with acceptable purity.

4.1.5.1.2. Derivatization

Even if the purification of 37-OPr proved to be critical in some respects, further derivatizations of this compound were nonetheless investigated. Compound 37-Mes was chosen as the first target molecule. We expected that the steric shielding offered from the mesityl substituent should yield a compound stable against hydrolysis, which would simplify the analysis and handling of the reaction product. Two different reaction sequences were tested (Fig. 147 and Fig. 149). The first method consisted of the direct reaction
between $37$-$O^{i}$Pr and a carbon-based nucleophile. In the second derivatization strategy, $37$-$O^{i}$Pr was firstly converted to the more reactive diarylboron halide $37$-$X$, which was then reacted with a suitable nucleophile.

Diarylalkoxy boranes are relatively weaker electrophiles compared to their halide analogs, and the isopropoxy substituent in compound $37$-$O^{i}$Pr offers a moderate steric shielding of the boron atom. For these two reasons, in the direct functionalization of $37$-$O^{i}$Pr, mesityllithium was employed as the nucleophile. This reagent is, in fact, more reactive compared to the analogous Grignard, zinc, or copper reagents. The reaction was performed on NMR scale by adding to a THF solution of the boron precursor MesLi as a solid at room temperature.

![Reaction scheme for the direct derivatization of compound $37$-$O^{i}$Pr.](image)

Upon addition of mesityllithium to the reaction mixture, the solution displayed a red fluorescence, and the in-situ NMR spectra of the reaction mixture confirmed the complete conversion of the starting material. After aqueous workup, the $^1$H NMR spectrum of the obtained crude mixture (Fig. 148) showed that the crude material was mainly constituted by one compound, and the solution displayed a light blue fluorescence. The comparison with the $^1$H NMR spectra of $37$-$O^{i}$Pr, confirmed the disappearance of the peaks assigned to the isopropyl moiety. Interestingly, also the signal at 8.09 ppm, assigned to the proton in ortho-position with respect to the boron center, could not be detected. Due to the low amount of material available for the reaction, no signal in the $^{11}$B NMR spectrum could be recorded, and therefore, no information about the nature and integrity of the boron center could be obtained. A definitive confirmation that the desired product had been synthesized was obtained only later by comparing the $^1$H NMR spectra of $37$-Mes obtained with the procedure in chapter 4.1.5.2.2.
Fig. 148 Comparison between the $^1$H NMR spectra of compound 37-OiPr (spectrum 1), of the crude mixture generated by the reaction between MesLi and 37-OiPr (spectrum 2), and of a pure sample of 37-Mes (spectrum 3). The solvent signal is marked with the symbol $\star$.

In the second derivatization pathway, 37-OiPr was firstly converted to compound 37-Br by using excess BBr₃. The obtained brominated derivative was then reacted with mesitylcopper(I). The higher electrophilic character on the boron atom in 37-Br allowed us to use a much milder nucleophile reagent in its derivatization. Mesitylcopper(I) had been mainly employed in the selective synthesis of mono or bis mesitylhaloboranes, where the stronger Grignard or organolithium reagents led to the generation of complex mixtures. Additionally, the solubility of this reagent in aromatic hydrocarbons constitutes a valuable characteristic in this reaction. Its lithium or magnesium analogs usually require ethereal solvents to be dissolved, which would react with the boron halides. The works published by the research group of Jäkle and coworkers are a clear example of the utility of this reagent in the derivatization of arylated bromoboranes with a mesityl or pentafluorophenyl substituent.

Fig. 149 Reaction scheme for the derivatization of compound 37-OiPr through the generation of compound 37-Br.
To generate compound 37-Br, compound 37-O\textsubscript{Pr} was treated with excess BBr\textsubscript{3} in toluene, at room temperature. The solvent and the excess of BBr\textsubscript{3} were removed under vacuum, and the crude material was washed with a mixture of hexane and toluene. The \textsuperscript{1}H NMR spectrum of the obtained product is reported in Fig. 150. As highlighted by the reported comparison, in the spectra of the reaction product, the signals belonging to the isopropyl moiety of compound 37-O\textsubscript{Pr} are not present. Additionally, the signal with the highest shift moved from 8.28 to 8.65 ppm. This signal was assigned to the protons in ortho-position with respect to the boron center, and its shift towards higher ppm is in accordance with the introduction of the more electron-withdrawing bromide substituent in place of the isopropoxy substituent.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{Comparison between the \textsuperscript{1}H NMR spectra of compound 37-O\textsubscript{Pr} (spectrum 1) and of the product obtained after addition of BBr\textsubscript{3} (spectrum 2). Signals marked with * protons in ortho-position with respect to the boron center. The signal marked with \textasteriskcentered was assigned to the proton located on the tertiary carbon of the isopropyl substituent in compound 37-O\textsubscript{Pr}. The solvent signal is marked with the symbol \textasteriskcentered.}
\end{figure}

Due to the high reactivity of boron halides, all attempts of crystallizing compound 37-Br only diminished the purity of the material. Therefore, the isolated compound was used directly in the following synthesis step. The crude material containing 37-Br was dissolved in C\textsubscript{6}D\textsubscript{6}, and MesCu was added at room temperature. After the addition, no changes in the NMR spectra could be detected, and only after heating the sample for 1 h at 60°C new signals could be observed. Complete conversion of the starting material (based on the complete disappearance of the signal at 8.65 ppm in the \textsuperscript{1}H NMR) was achieved after the sample was heated for two additional hours at 90°C. The reaction mixture was then subjected to aqueous workup, and the obtained crude material was characterized via NMR spectroscopy. In Fig. 151, the spectrum in CDCl\textsubscript{3} of the crude material (spectrum 1) is compared with the spectrum of the pure isolated 37-Mes\textsuperscript{[4.1.5.2]} (spectrum 2) obtained with the procedure reported later in chapter 4.1.5.2. The spectra show some correspondence between the signal in both the aromatic and the aliphatic region, suggesting that the target molecule could have been generated. Nonetheless, the nature of the byproduct generated, or
other aspects of this reaction were not further investigated since other synthesis paths with better performances had been established.

![NMR spectrum](image)

**Fig. 151** 1H NMR spectrum of the crude material, possibly containing compound 37-Mes (spectrum 1). 1H NMR spectrum of a pure sample of compound 37-Mes (spectrum 2). The solvent signal is marked with the symbol $\star$.

### 4.1.5.2. Compound 37-OH

Chronologically, 37-OH was firstly synthesized by the hydrolysis of 37-OiPr obtained with the method described in chapter 4.1.2.8. This method was inherently affected by the same downsides associated with the synthesis of 37-OiPr and, being compound 37-OH less readily derivatized than its isoproxy derivative, its reactivity was initially not examined. The borinic acid became an appealing starting material only when it could be reliably synthesized using the synthetic pathway discussed in chapter 4.1.3. The establishment of robust purification methods for this compound subsequently led to the development of the metalation procedure reported in chapter 4.1.2.8.1.

#### 4.1.5.2.1. Purification of 37-OH

The purification of compounds 134-OH and 135-OH showed that column chromatography using silica gel as the stationary phase could be employed for the purification of borinic acids. At the same time, as discussed for compound 135-OH, the strong interaction between the borinic acid and the silica gel could lead to an irreversible absorption that ultimately limits the efficiency of this purification method. Indeed, also 37-OH was affected by the same problematics when purification via column chromatography had been attempted. While pure samples of the compound could be obtained with this technique, only a small amount of the material subjected to purification could be recovered.

We, therefore, examined a frequently encountered procedure for the purification of simple borinic acids. This method is based on the formation of a complex between ethanolamine, or one of its derivatives, and the borinic acid itself. Such adducts are normally characterized by a high crystallinity and
low solubility and can be easily purified via crystallization or by performing washing cycles of the solid with appropriate solvents. To obtain the pure free borinic acid, the ethanolamine adduct can then be treated with acidic water followed by extraction with an organic solvent. In this process, the protonated ethanolamine remains in the aqueous phase, whereas organic solvents extract the desired product.

![Fig. 152 Formation of the complex between ethanolamine and the borinic acid 37-OH.](image)

The reaction between compound 37-OH and ethanolamine in THF yielded a white solid, which displayed a relatively low solubility in most common organic solvents. A brief solvent screening revealed that the material was reasonably soluble only in DMSO and in a DCM/methanol binary mixture. NMR analysis of the material performed with deuterated DMSO delivered spectra which suggested that the isolated substance may indeed correspond to compound 150; however, almost all the peaks displayed a broad shape, and the sum of their integral did not precisely correspond to the expected values. Single crystals suitable for x-ray diffraction analysis were obtained by layering with hexane a solution of the material in a 1/1 mixture of methanol/DCM. The solid-state structure obtained from the measurement, reported in Fig. 152, did not correspond to the expected borinate 150 but to compound 151 instead. Nonetheless, the result strongly suggested that the isolated material was indeed the desired compound prior to the dissolution in the DCM-methanol mixture. The presence of a large amount of methanol most likely led to the methanolysis of the B-O bond between the boron center and the oxygen atom of the ethanolamine ligand while the nitrogen atom remains bound to the boron center.

The low solubility of the ethanolamine adduct allowed us to develop a method for the isolation of pure 150 and consequently 37-OH also from mixture that contained high amounts of byproducts. Even stoichiometric amounts of anthracene did not interfere in the purification process, which motivated the establishment of the procedure described in chapter 4.1.1.7.1. The purification procedure consisted in treating the crude material dissolved in THF with a stoichiometric amount of ethanolamine, the so obtained precipitate was then washed several times with THF yielding pure 150. Hydrolysis of compound 150 in aqueous HCl proceeds quantitatively and yields pure 37-OH.
4.1.5.2.2. Derivatization

The borinic acid 37-OH itself cannot readily undergo substitution reactions which would replace the hydroxy functionality with an organic substituent. Therefore, 37-OH needed to be first converted to a more reactive species that could be further derivatized with suitable reactions. One of the derivatization pathways that could be adopted was the esterification of 37-OH with an alcohol to obtain a borinic acid ester analog to compound 37-OPr. Following this reaction path would have allowed us to use the already explored derivatization pathway described in the previous chapter 4.4.1.2. However, the susceptibility towards hydrolysis of 37-OPr motivated us to investigate alternative strategies.

We turned our attention to the compound class of potassium organofluoroborates. The synthesis of these compounds can be achieved starting from the corresponding borinic or boronic acid by the reaction with KHF₂ at room temperature, using methanol as the solvent. This long known compound family became increasingly popular since their first use in transition metal-catalyzed reaction was published. Potassium trifluoroborates had been found to be particularly useful reagents in the in Suzuki-Myaura cross-coupling since they showed to have some critical advantages over the classically employed boronic acids and boronic acid esters. Namely, their crystallinity, high stability, and monomeric nature. This last characteristic, in particular, facilitates their purification, storage, and handling. In some instances, the yields of the transition metal catalyzed coupling reactions were even improved when trifluoroborates were used instead of their borinic acid analogues. The use of fluoroborates is not limited to transition metal-catalyzed coupling reactions, but they could also be used as boron electrophiles in the reaction with lithium or Grignard reagents or as a source of nucleophilic fluoride. Additionally, they also react with trimethylsilyl chloride generating the corresponding fluoroboranes. This last reaction, in particular, attracted our attention since it allowed the smooth conversion of a stable and easy-to-purify species into a reactive one.
Therefore, we investigated if the synthesis of compound 37-Mes could be achieved starting from 37-OH through the generation of the potassium difluoroborate 37-F\textsubscript{2}K (Fig. 154). Firstly, 37-F\textsubscript{2}K was synthesized from 37-OH by reacting the borinic acid with KHF\textsubscript{2} in methanol. After recrystallization from ether, the desired compound was obtained with a yield of 69%. The potassium difluoroborate could then be derivatized using two different approaches analogously to what had been discussed in chapter 4.1.5.1.2. Compound 37-F\textsubscript{2}K could be either directly reacted with a suitable metalated reagent or be first converted to the more reactive species 37-F and then further reacted with a suitable reaction partner. In this thesis, only the second derivatization approach was investigated. The synthesis strategy is analogous to the one explored for 37-O\textsubscript{OPr}, in that a haloborane is firstly generated and then subsequently derivatized with a metallated reagent. However, one of the advantages of this synthesis sequence is the higher stability of compound 37-F\textsubscript{2}K. Practically, the experimental procedure involved the in-situ generation of compound 37-F via the reaction between 37-F\textsubscript{2}K and trimethylsilyl chloride in chloroform. After the excess trimethylsilyl chloride and the solvent were removed under vacuum, the obtained material was dissolved in benzene, and mesityllithium was added. After purification of the crude material via column chromatography and crystallization, compound 37-Mes was obtained in 22% yield with respect to compound 37-F\textsubscript{2}K.

Interestingly, the reaction between 37-F\textsubscript{2}K and trimethylsilyl chloride delivered a different outcome if THF was used as the solvent instead of chloroform. Directly after the addition of TMS-Cl, a complete conversion of 37-F\textsubscript{2}K to a new product was observed. The conversion of the starting material was reflected in a marked shift of the signals in the $^{11}$B and $^1$H spectra (Fig. 155). Namely, the $^{11}$B NMR signal shifted from 4.39 ppm to 39.62 ppm, and, in the $^{19}$F spectrum, two new signals at -106.84 and -158.40 ppm replaced the one observed for the starting material. It must also be mentioned that the shift of one of the newly observed signals corresponded with the one reported in the literature for TMS-F.\textsuperscript{356} We assumed this newly generated to be the THF adduct of compound 37-F, even though the signals observed in the $^{11}$B and $^{19}$F NMR spectra were not in agreement with the one reported for the few published analogous molecules. This difference may be possibly due to the different solvents employed in the NMR measurements. While the reaction performed in chloroform stopped at this stage, in THF, the generated compound subsequently fully converted into a second species within 24 h (Fig. 155). The signal recorded in the $^{11}$B NMR spectra shifted again, but in the opposite direction with respect to the first change. Namely, the maximum of the peak detected in the $^{11}$B NMR shifted from 39.62 to 24.78 ppm. In the fluorine spectrum, the signal of the fluorine atom attached to boron disappeared and only the signal assigned to

Fig. 154 Reactions sequence used for the synthesis of 37-Mes using the borinic acid 37-OH as the starting material and proceeding via the generation and derivatization of compound 37-F\textsubscript{2}K.
TMS-F could be detected. Concerning the $^1$H NMR spectrum, only few of the signals detected in the $^1$H NMR spectra underwent a change of their shift. Particularly relevant is the signal with the highest shift which changes its shift from 7.95 ppm to 8.03 ppm. Based on these observations, we speculated that the generated species corresponded to the THF adduct of compound 37-Cl.

![Fig. 155 Reaction between compound 37-F$_2$K and TMS-Cl in THF-d$_8$ monitored via $^1$H NMR spectroscopy. Spectrum 1, $^1$H NMR spectrum of compound 37-F$_2$K in THF-d$_8$. $^1$H NMR spectra, measured at different time intervals, of the same sample after the addition of TMS-Cl. Specifically, 1 h after the addition (spectrum 2), 2.5 h after the addition (spectrum 3), 4 h after the addition (spectrum 4), 24 h after the addition (spectrum 5).](image)

After removing the solvent and the excess of trimethylsilyl chloride under vacuum, the material was analyzed by means of NMR spectroscopy using C$_6$D$_6$ as the solvent. The collected data further supported the generation of compound 37-Cl. The signal detected at 57 ppm in the $^{11}$B NMR would correspond to the one reported in the literature for diarylchloroboranes. Additional hint was provided by comparing the $^1$H NMR spectrum of the obtained material with the spectra of compounds 37-O-iPr and 37-Br and considering the signal with the highest shift in particular. This doublet was associated with the proton in ortho position with respect to the boron atom, and its shift follows a trend that can be related to the Lewis acidity of the boron center (Fig. 156). This observation would confirm that the boron atom of the generated compound possesses a Lewis acidity which is in between the one of compound 37-Br and 37-O-iPr and supports the generation of compound 37-Cl. Reported examples that show a similar behavior are limited but a similar trend can be observed in the comparison between the $^1$H NMR data for 9,10-dichloro- and 9,10-dimethyl-9,10-diboranthracene reported by Kessler et al. For these two compound the signals assigned to the proton in ortho position with respect to the boron centers also display a higher shift for the compound with the more Lewis acidic boron center. However, the trend is not followed from the data of 9,10-dibromo-9,10-dihydro-9,10-boranthracene reported by Bieller et al.
Fig. 156 Comparison between the $^1$H NMR spectra of compounds 37-O$^\text{Pr}$ (spectrum 1), 37-Cl (spectrum 1) and 37-Br (spectrum 3). The shift of the signal at the highest shift may be a tool to estimate the Lewis acidity of the boron of this class of compounds.

To confirm the generation of compound 37-Cl, a more extensive characterization of the compound should be performed. However, for the scope of this work, the synthesis of 37-Cl was not necessary since 37-F showed to be a suitable reaction partner in the reaction with mesityllithium. Moreover, 37-Cl is more sensitive toward hydrolysis, and it could also participate in ether cleavage reactions which did not render this species more appealing than its fluoride analog.

4.1.5.3. Summary

In the course of this chapter, it was investigated the purification of compound 37-OH, synthesized via the methods reported in chapter 4.1.2 or 4.1.3 and of compounds 37-O$^\text{Pr}$, synthesized via the method reported in chapter 4.1.2

Thanks to the low solubility of the adduct formed between compound 37-OH and ethanolamine, it was possible to establish a robust and effective procedure for the purification of the borinic acid derivative. The method relied on the precipitation of the adduct and extraction of the impurities with a suitable solvent. This alternative was preferred to standard chromatographic techniques since the affinity of borinic or boronic acid with the stationary phase could lead to irreversible absorption of the compound on the column and, therefore, cause material loss. Additionally, the chemical stability of compound 37-OH in comparison to its ester simplified the handling of the compound and the choice of the purification conditions. In contrast, the sensitivity towards hydrolysis of compound 37-O$^\text{Pr}$, occasionally led to the cleavage of the isopropoxy substituent during the purification process and the borinic acid was isolated instead. In addition, the low reproducibility of the reaction used for the generation of compound 37-O$^\text{Pr}$ hindered the establishment of a standard and reliable purification procedure, and the desired compound was obtained with an acceptable purity in only one instance. Relying on the in-situ generation of Mg$^+$, as reported in chapter 4.1.2.7.14.1.2.8.1, would have most likely improved the reproducibility of the
synthesis of compound 37-O\textsuperscript{i}Pr. However, this procedure implies the presence of a stoichiometric amount of anthracene in the final crude mixture, and selective removal of this byproduct is difficult to achieve without inducing the cleavage of the isopropoxy substituent. A more suitable method to obtain derivative 37-O\textsuperscript{i}Pr in a pure form is possibly represented by the esterification of a pure sample of compound 37-OH with isopropanol.

The second aim of this chapter was the development of synthesis procedures that would allow the substitution of the hydroxy and isopropoxy substituent with a mesityl residue in compounds 37-OH and 37-O\textsuperscript{i}Pr, respectively. Derivatization of compound 37-OH was achieved by firstly converting the borinic acid to the benchtop-stable potassium difluoroborate salt 37-F\textsubscript{2}K. Then, the addition of TMS-Cl to compound 37-F\textsubscript{2}K led to the in-situ generation of compound 37-F, which was finally reacted with mesityllithium to afford the desired derivative 37-Mes. The substitution of the isopropoxy substituent of compound 37-O\textsuperscript{i}Pr was attempted with two different approaches. The first one involved the direct reaction with mesityllithium, and the second a two-step synthesis sequence. In this second approach, the isopropoxy substituent was firstly substituted with the more reactive bromide substituent via the reaction with BBr\textsubscript{3}. The generated bromoborane was then reacted with mesitylcopper(I). Both synthesis sequences delivered a crude mixture in which the desired product could be detected; however, a pure sample of the targeted compound was not isolated following these two strategies. The small amount of compound 37-O\textsuperscript{i}Pr in our hands limited the investigation and the optimization of the illustrated reactions. Therefore, we could draw only partial conclusions regarding the derivatization of this compound. As mentioned above, the borinic acid ester could be also generated via esterification from 37-OH and then used in the derivatization sequences reported for this compound. However, this synthesis strategy was not investigated since it did not present considerable advantages with respect to the derivatization procedure established for 37-OH.

The analysis reported in this chapter clearly shows how compound 37-OH represents the best candidate precursor for the synthesis of this family of compounds. The borinic acid could be easily isolated, purified and the developed derivatization pathway allowed the substitution of the hydroxyl group with a mesityl substituent. The same synthesis sequence can be potentially applied to the generation of other organoborane derivatives, which fulfills one of the most important requirements set in the aim of this thesis. Additionally, the potassium difluoroborate salt 37-F\textsubscript{2}K synthesized as an intermediate in the derivatization process can also be used as a stable storing form from which different derivatives can be generated.
4.1.6. Conclusions and synthetic path of choice

After the different synthesis strategies had been put into practice, a general examination of the two successful synthesis approaches described in chapter 4.1.2 and 4.1.3 was needed to assess which pathway was the most suitable for the construction of the molecular scaffold. The two synthesis sequences were compared by setting 37-OH as the target compound since this was recognized as the most suitable precursor for the synthesis of further derivatives.

Both synthesis paths, in which the boron center was introduced via electrophilic trapping of a metallated intermediated, successfully led to the construction of the desired molecular scaffold. In the two reaction sequences, the boron center was introduced in the molecular backbone either at the beginning (chapter 4.1.3) or at the end of the synthesis sequence (chapter 4.1.2). The two synthesis routes shared some strong similarities in terms of the reactions used to assemble the molecular structure. However, introducing the boron center at different stages introduces limitations on the reaction and purification conditions that could be applied.

In Fig. 157 the two different reaction sequences are compared, and the yield for every step is reported. The two different pathways display a very similar overall yield if the depicted procedures are considered. It must be considered, however, that for the synthesis of compounds 121 and 133, many reaction procedures are known, and no extensive study was performed to identify the most efficient procedure and optimize the generation of these compounds. Therefore, an improvement of the overall reaction yield may be achieved by improving the efficiency of these initial steps. A side aspect that could also be improved is the reactions leading to compound 133. Despite being practically advantageous, the method presents a particularly low atom economy that could be improved by adopting another reaction procedure.

One of the crucial differences between the two sequences lies in the purification condition used for the isolation of the different compounds. Specifically, both 134-OH and 135-OH were purified via column chromatography, and the chromatographic procedure for compound 135-OH involved a rather time-consuming and elaborated protocol which negatively influenced the yield of the reaction. Conversely, all the compounds of the second reaction sequence can be purified either via distillation (compound 121 and 123-Cl) or via crystallization. This critical difference influence the practicability, the cost, and the ease of upscaling the entire process. For the above-mentioned reasons, the synthesis route where the boron center is introduced at the last stage is considered the more efficient and preferred pathway.
Fig. 157 Comparative overview of the two developed synthesis sequences towards compound 37-OH.
4.2. Solid-state structure

X-ray diffraction analysis of suitable single crystals delivered the solid-state structures of the borinic acid 37-OH and the mesityl derivative 37-Mes as well as the solid-state structures of compounds 151 and 137-Si. At the time of writing, no solid-state structures that presents the same central molecular framework of compound 37-R or 137-Si have been reported in the literature. Specifically, no example with a carbon-based spiro center and nitrogen and boron (or silicon) atom at the external vertices of the two six-membered spiro cycles have been published. In particular, such molecular arrangement, with the combination of nitrogen and boron as the two heteroatoms, has been reported only in 7 patents. Among the reported solid-state structures, compound 154 was the example that displayed the highest structural similarity with 37-R (Fig. 158). The only difference between the two molecular scaffolds was represented by the sulfone moiety of compound 154 replacing the borylene fragment of compound 37-R. It follows that the solid-state structure of compound 154 could not be used to discuss the structural parameter concerning the boron center, but it still is a valid element of comparison for the other structural parameters. In this chapter, we additionally included compounds 152, 134-OH, 153, 155, 156, 157 and 158 as additional elements of comparison (Fig. 158). The latter six compounds have been previously reported in the literature, whereas Compound 152 was synthesized by Valerij Kupreenko during the execution of a master thesis project in our research group.

![Molecular structures of the compounds used as element of comparison in the discussion of the solid-state structure of 37-OH, 37-Mes, 137-Si and 151.](image)

To compare the different solid-state structures and evaluate the relative arrangement of the fragments at the two sides of the spiro center six angles and two planes were defined according to the scheme reported in Fig. 159 and Fig. 162. The values of these and other relevant structure parameters for the above-mentioned structures are summarized in Table 17, Table 18, and in Table 29 in the Appendix section.
Fig. 159 ORTEP representing the solid state structure of compound 37-OH. The angles α, spiro α, δ, and spiro δ have been particularly named to help referring to them in the course of the following description. The same names apply also to compound 137-Si the only difference being that in this compound the silicon atom is at the vertex of the angle α. Plane Δ is defined as the best plane passing from the atom of the spiro cycle containing the nitrogen heteroatom. Similarly, plane A is defined as the best plane passing from the atom of the spiro cycle containing the boron or silicon heteroatom. Hydrogen atoms are omitted for clarity.

4.2.1. Packing

In the solid structures of compounds 37-Mes, the molecules are arranged into layers that are parallel to the best plane of the boryl bridge and its three substituent and perpendicular to the best plane of the spiro ring at the acceptor (Fig. 160). Within one layer, the molecules have the same orientation, with the donor-acceptor vector pointing in the same direction. In the following layer, the molecules’ orientation changes with the donor-acceptor vector pointing in the opposite direction. This alternated motif is present throughout the whole structure. Also, the planes are pairwisely interlocked via the interaction between the bent donor moieties of two molecules belonging to two consecutive layers.

Similarly, in the solid-state structure of compound 137-Si, the molecules are arranged with an alternate orientation, and the packing motif resembles the one observed for compound 37-Mes. In the solid-state structure of compound 37-OH, molecules with the same orientation are ordered in rows in a staggered arrangement, and the orientation of the molecules is inverted in the following row. The arrangement is iterated throughout the structure, and the same structural motif is repeated perpendicularly to these rows with an inclination.
Fig. 160 Molecular arrangement in the crystal lattice of compounds 37-Mes (top) and 37-OH (bottom), hydrogen atoms are omitted for clarity.

In the solid structure of compound 151, the molecules are arranged in dimers instead. The acceptor fragments of two different units are bridged by two methanol molecules which interact via hydrogen bonding with the substituent at the boron center (Fig. 161). An analogous situation is observed in the case of compound 152, where two lithium atoms bridge the borohydride fragments of two molecules.
4.2.2. Bond lengths and angles

For all the compounds, the observed bond lengths were comparable with the ones of the selected comparison examples. The C-N bond lengths did not change considerably between the examined examples, and consistently the length of the bond between the nitrogen atom and the phenyl substituent was always longer than the remaining two C-N bonds. The measured values range between 1.437(3) and 1.4418(14) Å for the bond between the nitrogen and the phenyl substituent and between 1.4014(33) and 1.4137(15) Å for the bonds between nitrogen and the central molecular scaffold. A low variation was also observed for the length of the C-C bonds at the spiro center, which ranges between 1.5329(23) and 1.555(2) Å. The exchange of the hydroxy substituent of compound 37-OH with the mesityl fragment in compound 37-Mes only has a negligible effect on the length of the B-C bonds. A greater change, albeit still quite small, is observed in compound 151 where the coordination of ethanolamine causes an increase in the B-C bond length of about 0.05 Å. Such effect, with the same magnitude, is also observed for other pairs of borinic acid and their corresponding ethanolamine adduct. For instance In diphenyl borinic acid, the length of the B-C bonds changes from 1.5695(1) Å and 1.5642(1) Å to 1.6136(1) Å and 1.6277(1) Å after the formation of the adduct with 2-dimethylamino-ethanol. In compound 137-Si, the length of the bonds between the silicon heteroatom and the molecular scaffold are slightly shorter than the one between the silicon atom and the two methyl groups. The same difference in the order of 0.01 Å was also observed for compounds 157 and 158. In compound 156, all four bonds shared the same length instead.

The values for the angles that have the spiro center as the vertex covered a relatively wide range and varied between 105.63(14)° to 115.2(2)°. In each molecule, the highest value was consistently observed.
for the angle spiro $\alpha$ and always exceeded the value expected for a tetrahedral geometry. These angles measured approximately 115° in the compounds with a boron atom and 118.61(15)° in compound 137-Si. Instead, the angle spiro $\delta$ showed values closer to the one expected for a tetrasubstituted carbon atom and varied between 110.57(10)° and 111.0(2)°.

The angles that have the boron atom at the vertex changed in accordance with the hybridization of the heteroatom. For compounds 37-Mes and 37-OH, where the boron atom is tricoordinated, they approached the theoretical value of 120°, measuring between 117.05(10)° and 124.0(2)°. In both molecules, the sum of these angles yielded the expected value of 360°. In compound 151, where the boron atom is tetracoordinated, the angles displayed lower values and ranged from 98.15(9)° to 113.37(11)°. In this compound, the particularly low value of 98.15(9)° corresponds to the N-B-O angle, and its low volume is induced by the structural constraints introduced by the dimeric arrangement.

If only the values of angle $\alpha$ are considered, the lowest value was measured for compound 137-Si (104.02(8)). This value matches the one measured for the internal angle of compound 156, and it is only 3° greater than the one observed in compounds 157 and 158. For the boron-based compounds, the values of $\alpha$ were contained in a relatively small range and yielded the values of 112.04(10)°, 117.05(10)° and 118.2(2)° for compounds 151, 37-Mes and 37-OH, respectively.

The angles with the nitrogen atom at the vertex displayed similar values in all the newly obtained structures and matched the values measured in the comparison examples. In all molecules, the angles approached the ideal values expected for an atom with a trigonal geometry of 120°, and their sum yielded in all cases values close to 360°. In all the molecules, angle $\delta$ displayed values slightly over 120°, whereas the other two angles with nitrogen at the vertex yielded values slightly lower than 120°. The same trend was consistently observed in the comparison examples.

**4.2.3. Donor and acceptor planarity and relative arrangement**

This section discusses the planarity of the two molecular fragments separated by the spiro center and their relative arrangements in space. For the structures containing a boron heteroatom, these two parameters are of interest due to their influence on the photophysical properties of the emitters. As already mentioned in this thesis, the relative spatial arrangement of the donor and acceptor fragments has an important influence on the TADF performance of the chromophores and constitutes a critical structural parameter for these compounds.

The donor and acceptor moieties of all the three boron-based compounds are planar. The maximum deviation from the best plane of the donor fragment was measured for compound 151 (0.2182(13) Å). In contrast, the maximum deviation from the best plane of the acceptor fragment was measured for compound 37-Mes (0.1384(12) Å). In contrast to what has been reported for the class of compound spiro-B in chapter 3.3, the donor fragments of the analyzed molecules showed only a moderate fold along the N-C(spiro) vector. The maximum value of the donor folding angle (measured as described in chapter 3.3) was observed for compound 37-Mes, which displayed a value of 10.342(61)°. In this class of emitters, also the acceptor fragment is based on a 6-membered spiro ring which renders this moiety less rigid than the one of the emitters belonging to the class spiro-B. A fold of the acceptor fragment along the B-C(spiro) vector was expected and was indeed observed with a different magnitude for all the analyzed molecules. The highest value was measured for compound 151 and corresponded to 6.134(73)°. Nonetheless, this
result is considerably lower than the one displayed by compound 152 (16.323(96)°). The compound that showed the least folded donor and acceptor fragments was 37-OH which yielded the values of 3.371(108)° and 4.839(193)° for the folding angles of donor and acceptor moiety, respectively.

By the analysis of the obtained solid-state structures, we could also assess whether the targeted molecular architecture would ensure the desired orthogonal arrangement between the donor and acceptor moieties. To evaluate this aspect, we measured three different angles, the one between the best planes of the spiro and acceptor fragments (A and Δ, Fig. 159) and the two tilt angles reported in Fig. 162. The donor tilt angle was defined as the angle between the best plane of the acceptor moiety and the vector passing from the spiro center and the heteroatom of the acceptor fragment. Similarly, the acceptor tilt angle was defined as the angle between the best plane of the donor moiety and the vector passing from the spiro center and the heteroatom of the donor fragment. These angles provided information about the reciprocal tilting of the moieties within their planes.

The analysis of these values showed that, indeed, the integration of a spiro center in the molecular geometry ensures an almost perfectly orthogonal arrangement between the donor and acceptor fragments (Fig. 159). The measurement of the angle between A and Δ yielded the values of 87.198(17)°, 87.679(54)° and 89.867(150)° for compounds 37-Mes, 151, and 37-OH, respectively. However, the donor and the acceptor moieties are slightly bent towards each other within their respective planes, which is particularly visible in the solid-state structure of compound 37-Mes (Fig. 162).
Fig. 162 Solid-state structure of compound 37-Mes seen from two different orientations a) perpendicular to the best plane of the acceptor moiety and b) perpendicular to the best plane of the donor moiety. The solid lines correspond to the vector passing from the heteroatom and the spiro center. The dashed lines correspond to the edge of the best plane of the acceptor or donor moiety. The color green is used to describe the geometric element associated with the acceptor, and the color blue is used to describe the geometric element associated to the donor. The donor tilt angle is defined as the angle between the acceptor best plane (for compound 137-Si, the best plane of the fragment containing the silicon atom) and the N-C(spiro) vector. The acceptor tilt angle is defined as the angle between the donor best plane and the vector passing through the spiro center and the boron atom (or silicon atom for compound 137-Si).

Indeed, compound 37-Mes yielded the values of 12.735(33)° and 9.495(38)° for the acceptor and donor tilt angles, respectively. In contrast, compound 37-OH displayed a minor tilt of the two moieties, confirmed by the low values of 0.915(61)° and 4.067(55)° for the acceptor and donor tilt angles, respectively. Interestingly, compound 151 showed a nearly zero value for the donor tilt angle (0.04(36)°) but a value of 14.35(45)° for the acceptor tilt angle, which was also the highest value for this parameter measured for these compounds. In the solid structure of compound 37-Mes the tilting of the donor and acceptor moiety is possibly induced by the establishment of CH-π interaction between two distinct molecules in the crystal lattice as represented in Fig. 163. The length and characteristics angles of these interactions, listed in Fig. 163, are comparable with reported values for similar CH-π interactions found in the literature.373, 374 The weak nature of these interactions is most likely influencing the molecular structure only in the solid-state, and a different situation is present in solution.375 In compound 151 instead, the tilt of the acceptor is caused by the incorporation of dichloromethane in the crystal lattice, which intercalates between two acceptor moieties of two different dimers.

In the solid-state structures of the silicon-based compound 137-Si the two molecular fragments separated by the spiro center are also planar. They show two low folding angles which are similar in value, namely, 5.008(91)° and 4.909(75)° for the fragment containing the nitrogen heteroatom and the silicon heteroatom, respectively. The relative arrangement of the two fragments is qualitatively similar to the
one observed for compound 37-Mes. The two compounds share, in fact, a similar packing arrangement, and both displayed a similar CH-π interaction between the molecules in the crystal lattice. The angle between the two planes A and Δ measured 88.668(261)°, which is even more closed to the ideal value of 90° for a perfect orthogonal geometry than the one measured for 37-Mes. Similarly to compound 37-Mes, the two molecular fragments are tilted respect to each other within their planes but less markedly. The donor and the “acceptor” folding angles yielded the values of 7.995 (47)° and 1.908 (52)°, respectively, where for acceptor fragment was considered the fragment with the silicon heteroatom to maintain the analogy with the other structures.

**Fig. 163** Sections of the crystal lattice of 37-Mes that highlights the identified CH-π interactions between different molecules in the crystal lattice. The reported lengths refer to the distances between the hydrogen atom and the centroid (indicated with •) of the interactive aromatic ring.

### 4.2.4. Summary

In summary, the analysis of the obtained solid-state structures confirmed that the presence of a spiro center in the molecular structure successfully renders the acceptor and donor moiety almost orthogonal, one respect to the other. In contrast to what had been observed in chapter 3.3.1, the donor moiety of the analyzed compounds is not subjected to a strong fold. On the other hand, the six-membered spiro-ring at the acceptor fragment renders this moiety more flexible compared to the acceptor fragments of the
emitters of the class spiro-B. Consequently, small folding angles could also be measured for this portion of the molecule. In the solid structure, the acceptor and donor moieties are also tilted within their planes. However, these variations from the perfect orthogonal arrangement are caused by interaction in the crystal lattice and do not persist in solution as suggested by the number of signals present in the $^1$H and $^{13}$C NMR spectra of these compounds. A bent and asymmetric structure would have produced more complex spectra with a higher number of signals.

<table>
<thead>
<tr>
<th></th>
<th>37-Mes</th>
<th>37-OH</th>
<th>151</th>
<th>137-Si</th>
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<tbody>
<tr>
<td><strong>Bond lengths</strong> (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-C$^a$</td>
<td>1.5481(16)</td>
<td>1.556(4)</td>
<td>1.6045(19)</td>
<td>1.8522(19) (Si-C)</td>
</tr>
<tr>
<td></td>
<td>1.5425(17)</td>
<td>1.546(4)</td>
<td>1.6045(20)</td>
<td>1.8553(19) (Si-C)</td>
</tr>
<tr>
<td>B-R</td>
<td>1.5777(16)</td>
<td>1.366(4)</td>
<td>1.4956(17) (B-O)</td>
<td>1.865(2) (Si-C)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>1.6204(18) (B-N)</td>
<td>1.869(2) (Si-C)</td>
</tr>
<tr>
<td>N-C$^b$</td>
<td>1.4017(17)</td>
<td>1.4017(17)</td>
<td>1.4044(17)</td>
<td>1.403(2)</td>
</tr>
<tr>
<td></td>
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<td>1.4044(17)</td>
<td>1.4017(17)</td>
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<tr>
<td>N-Ph</td>
<td>1.4400(16)</td>
<td>1.437(3)</td>
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<td><strong>Angles</strong> (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Between A and D</td>
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<td>89.867(150)</td>
<td>87.679(54)</td>
<td>88.668(261)</td>
</tr>
<tr>
<td>α</td>
<td>117.05(10)</td>
<td>118.2(2)</td>
<td>112.04(10)</td>
<td>104.02(8) (C-Si-C)</td>
</tr>
<tr>
<td>δ</td>
<td>121.08(9)</td>
<td>121.6(2)</td>
<td>121.41(11)</td>
<td>121.68(15)</td>
</tr>
<tr>
<td>spiro α</td>
<td>115.02(9)</td>
<td>115.5(2)</td>
<td>115.2(1)</td>
<td>118.61(15)</td>
</tr>
<tr>
<td>spiro δ</td>
<td>110.68(9)</td>
<td>111.0(2)</td>
<td>110.57(10)</td>
<td>111.05(14)</td>
</tr>
<tr>
<td>Acceptor folding</td>
<td>5.645(46)</td>
<td>4.839(193)</td>
<td>6.134(73)</td>
<td>4.909(75)</td>
</tr>
<tr>
<td>Donor folding</td>
<td>10.342(61)</td>
<td>3.371(108)</td>
<td>7.257(63)</td>
<td>5.008(91)</td>
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<td>Acceptor tilt angle</td>
<td>12.735(33)</td>
<td>0.915(61)</td>
<td>14.35(45)</td>
<td>7.995 (47)</td>
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<td>Donor tilt angle</td>
<td>9.495(38)</td>
<td>4.067(55)</td>
<td>0.04(36)</td>
<td>1.908 (52)</td>
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</tbody>
</table>

Table 17 Selected structural parameters measured for the solid-state structures obtained in this thesis. $^a$ Bonds between the boron (or silicon) atom and the main molecular scaffold. $^b$ Bonds between the nitrogen atom and the main molecular scaffold.
<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
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<th>153</th>
<th>154</th>
<th>155</th>
<th>134-OH</th>
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<tr>
<td>B-Ca</td>
<td>1.590(5)</td>
<td>1.5436(1)</td>
<td>1.757(2) (S-C)</td>
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<td>1.554(2)</td>
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<td></td>
<td>1.587(5)</td>
<td>1.5485(1)</td>
<td>1.753(2) (S-C)</td>
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<td>1.554(2)</td>
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<td>B-R</td>
<td>1.1370(335) (B-H)</td>
<td>1.5711(2)</td>
<td>1.434(2) (S-O)</td>
<td>-</td>
<td>1.373(4)</td>
</tr>
<tr>
<td></td>
<td>1.1295(453) (B-H)</td>
<td>-</td>
<td>1.440(2) (S-O)</td>
<td>-</td>
<td>-</td>
</tr>
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<td>N-Cb</td>
<td>1.398(4)</td>
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<td>1.402(3)</td>
<td>1.405(3)</td>
<td>-</td>
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<tr>
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<td>1.402(4)</td>
<td>-</td>
<td>1.418(3)</td>
<td>1.403(3)</td>
<td>-</td>
</tr>
<tr>
<td>N-Ph</td>
<td>1.452(4)</td>
<td>-</td>
<td>1.435(3)</td>
<td>1.442(3)</td>
<td>-</td>
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</table>

<table>
<thead>
<tr>
<th>Angles (°)</th>
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<th>153</th>
<th>154</th>
<th>155</th>
<th>134-OH</th>
</tr>
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<tr>
<td>between A and Δ</td>
<td>87.84(10)</td>
<td>-</td>
<td>88.376 (87)</td>
<td>89.858(70)</td>
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<tr>
<td>α</td>
<td>113.3(3)</td>
<td>116.729(5)</td>
<td>104.26(11) (C-S-C)</td>
<td>-</td>
<td>118.8(2)</td>
</tr>
<tr>
<td>δ</td>
<td>122.0(3)</td>
<td>-</td>
<td>121.04(19)</td>
<td>120.51(17)</td>
<td>-</td>
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<tr>
<td>spiro α</td>
<td>114.8(2)</td>
<td>116.840(5)</td>
<td>115.11(18)</td>
<td>100.74(15)</td>
<td>118.6(2)</td>
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<td>spiro δ</td>
<td>110.2(2)</td>
<td>106.857(6)</td>
<td>111.26(18)</td>
<td>110.80(16)</td>
<td>-</td>
</tr>
<tr>
<td>acceptor folding</td>
<td>16.323(96)</td>
<td>4.115</td>
<td>11.330(96)</td>
<td>3.964(69)</td>
<td>0.742(75)</td>
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<tr>
<td>donor folding</td>
<td>7.297(112)</td>
<td>-</td>
<td>3.321(100)</td>
<td>15.818(81)</td>
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<tr>
<td>acceptor tilt angle</td>
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<td>5.969(74)</td>
<td>-</td>
<td>10.438 (60)</td>
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</table>

Table 18 Selected structural parameters measured for the solid-state structures as the examples used as a comparison. a Bonds between the boron (or silicon) atom and the main molecular scaffold. b Bonds between the nitrogen atom and the main molecular scaffold.
4.3. Photophysical properties

In the context of this thesis, it was possible to analyze only the photophysical properties of compound 37-Mes in solutions. Even if limited, these measurements were sufficient to confirm the achievement of one of the aims of this work. Specifically, we could evaluate whether the newly synthesized chromophore would display TADF, as observed in compound 32, and how its photophysical properties compare to the related emitter.

We hypothesized that the photophysical characteristic of compounds 37-Mes and 32 would display strong similarities. Specifically, we expected the fluorescence emission of 37-Mes, to originate from a charge-transfer excited state (CT) and that the presence of oxygen would strongly influence its intensity and lifetime. By studying the impact of oxygen on the emission profile and the excited state lifetime we intended to confirm the involvement of triplet states in the emission process and, therefore, the emission via TADF.

The molecular structure of compounds 37-Mes differs from the one of compound 32 solely for the presence of an arylated borylene bridge in place of the carbonyl group at the acceptor fragment. By comparing these two compounds, we could therefore isolate the effect that this structural difference has on the photophysical properties of the emitter. In donor-acceptor systems, the two frontier orbitals, HOMO and LUMO, are strongly localized on the donor and acceptor moiety, respectively. Therefore, a foreseeable effect of the structural change at the acceptor was the modification of the fragment electronic properties which would then cause an alteration of the HOMO-LUMO energy difference and produce a shift of the emission wavelength.

Modification of the acceptor fragment could also induce a change of the energy associated with the locally-excited state centered on the acceptor. As already remarked several times in this thesis, locally-excited states play a crucial role in the delayed emission of a TADF chromophore (1.3.1.2). Indeed, Monkman and co-workers demonstrated that a locally-excited state centered on the acceptor has a critical role in the TADF emission of 32 (chapter 1.3.2.2). By employing solvents with different polarities in their measurements, the authors could modify the energy difference between the charge-transfer and the acceptor-centered excited states. The alteration of the energy difference between the two states influenced the rate of the rISC process and consequently the efficiency of the delayed emission. Likewise, the introduction of the boron center in place of the carbonyl group at the acceptor fragment of 32 might alter the above-mentioned energy difference and, therefore, the efficiency of the TADF emission. One of the aims related to this class of emitters that could not be verified was whether the change of the substituent at the boron center could be indeed used to tune the emission wavelength of the chromophores. Different derivatives should be prepared, and their photophysical properties should be characterized to verify the relationship between the substituent R installed in the structure and the fluorescence emission of compounds 37-R.

Compound 37-Mes was characterized by means of absorption and fluorescence spectroscopy as described in chapter 3.4 for compounds of the class spiro-B. TCSPC measurements were used to determine the excited state lifetimes and to confirm the involvement of triplet excited states in the chromophores’ emission. The emitters’ solutions were prepared using both toluene and THF and allowed us to investigate the influence of the solvent polarity on the examined photophysical properties. The
experimental procedures adopted for the measurement were analogous to the one presented in chapter 3.4.

4.3.1. Absorption and emission spectroscopy

The absorption spectra of the THF and toluene solutions of compound 37-Mes are almost identical (Fig. 164). They both present a marked peak at 285 nm with two shoulders at 304 nm and 320 nm. In the range between 295 and 345 nm, the two spectra resemble the one obtained for of compound 32 but also the absorption spectra of 9-mesityl-9,10-dihydro-9-bora-anthracene. In the emission spectra, only one peak was observed, and the wavelength associated with the emission maximum showed to be dependent from the solvent employed in the measurement. Namely, the emission maxima were detected at 467 nm and 495 nm in the measurement of the toluene and THF solution, respectively. The observed peaks were broad, without a fine structure and characterized by a large Stokes shift in both cases. The energy difference between the peak maximum in the absorption spectra and the peak maximum in the emission spectra accounted for 13674 cm⁻¹ and 14885 cm⁻¹ for the measurements in toluene and THF, respectively.

![Normalized absorption and emission spectra of compound 37-Mes in two different solvents. Green line, measurements performed in THF. Blue line, measurements performed in toluene. The absorption spectra were measured under atmospheric conditions whereas the emission spectra were recorded in absence of air.](image)

The observation of positive solvatochromism in the emission measurements, the Gaussian shape of the emission peaks, and the large Stokes shift strongly indicate that the observed emission occurs from a charge-transfer excited stated (CT). Conversely, the solvent polarity did not influence the absorption spectra, suggesting that the absorption of light initially produces a locally-excited state, which converts into the charge transfer excited state responsible for the emission. The same behavior had also been observed for the compounds of class spiro-B (chapter 3.4) and for 32 itself.\(^{84}\)

The exclusion of air from the sample caused a significant increase in the emission intensity, indicating the involvement of triplet excited states in the radiative process. On the other hand, degassing the sample did not cause any marked change of the emission wavelength or the peak shape, suggesting that the transition took place from the same excited state under both conditions. The only difference that could be detected between the two emission spectra was the presence of a shoulder at the low-wavelength
extreme of the emission peak measured for the aerated toluene solution (Fig. 165). In the study of the photophysical properties of 32, in addition to the main emission peak generated by the decay of the CT excited state, two additional emission bands were observed. The peak with emission maximum at 350 nm was assigned to the emission from a locally-excited state located at the acridine fragment, whereas the structured band at 412 nm to the emission from a locally-excited state located at the anthracenone acceptor unit. Therefore, we supposed that the additional emission peak observed for compound 37-Mes is generated by the radiative decay of a locally-excited state centered at either the donor or acceptor fragment. The emission maximum of the observed shoulder was detected at 400 nm, which did not match the emission band attributed to the acridine fragment. However, this value almost perfectly corresponded to the emission maximum of 405 nm displayed by 9-mesityl-9,10-dihydro-9-bora-anthracene. The detected additional band could therefore be generated by the radiative decay of the excited state centered on the boron-based acceptor fragment.

It is also worth mentioning that the excitation spectra measured at the emission maxima followed, in both solvents, the same trend of the absorption spectra confirming the connection between the absorption and the recorded emission. Absorption and emission spectra only slightly differed for their onsets which for the excitation spectra were shifted of about 100 cm$^{-1}$ towards higher energies in both solutions.

![Fig. 165 Comparison between the fluorescence emission spectra of compound 37-Mes in toluene solution measured in presence of air (green line) and in the absence of air (blue line).](image)

The main emission peak recorded for 32 in toluene solution also presented structureless and broad shape characterized by a large Stokes shift. However, the emission maximum for this chromophore was detected at 510 nm, which is red-shifted by about 43 nm (1805 cm$^{-1}$) with respect to the one of compound 37-Mes in the same solvent. This observation implies that the HOMO-LUMO energy difference in compound 37-Mes is greater than in compound 32. As previously mentioned, the two emitters share the same molecular scaffold except for the structural modification of the acceptor fragment. The energy
difference between the two emission maxima could be therefore caused only by the substitution of the carbonyl group in compound 32 with the aryl-substituted borylene bridge in compound 37-Mes. Since we expected the frontier orbitals to be separately localized on the donor and acceptor fragment of the molecule, we could assume that the energy associated with the HOMO centered on the donor fragment did not change considerably between the two emitters. From these considerations, it follows that the LUMO in compound 37-Mes has a higher energy than the LUMO of 32 and that the boron-based acceptor fragment has a lower acceptor strength compared to the carbonyl-based fragment. However, to definitely confirm this hypothesis, the electrochemical characterization of the two emitters and the calculation of their orbital’s energy should be performed. In the effort to perform a qualitative comparison of the two acceptor fragments and highlight their different electron-accepting abilities we collected the reduction potential for benzophenone and for diphenylmesitylborane reported in the literature. For the measurements performed in DMF, more negative values were observed for the organoboron compound. Specifically, -1.79 V for diphenylmesitylborane and -1.72 V and -1.776 V for benzophenone.³⁷⁷-³⁷⁹ It must be additionally noted that even more cathodic reduction potentials (between -2.21 V and -2.41 V) had been reported for triphenylborane analyzed in THF.³⁸⁰ This first analysis could partially confirm the weaker accepting nature of the boron-based fragment compared to the one based on benzophenone. Nonetheless, a proper conclusion can be drawn only by the analysis of the complete chromophores.

### 4.3.2. Excited state lifetime and conclusions

The values obtained from the excited state lifetime measurements are summarized in Table 19 together with the values measured by Monkman and co-workers for 32.³⁸⁴ The analyses were performed both in the presence and absence of air and using both THF and toluene solutions of the emitter. Independently from the solvent used, the exclusion of air from the sample had a marked influence on the recorded lifetimes, exemplified by the transient decays for the toluene solution reported in Fig. 166.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Measurement under air (fractional intensities)</th>
<th>Measurements under vacuum (fractional intensities)</th>
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</thead>
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<tr>
<td>37-Mes⁴</td>
<td>Toluene</td>
<td>2.7 ns (1); 35.2 ns (99)</td>
<td>0.223 µs (19); 7.8 µs (81)</td>
</tr>
<tr>
<td>37-Mes⁴</td>
<td>THF</td>
<td>7.8 ns (4); 44.2 ns (96)</td>
<td>0.25 µs (17); 5.84 µs (83)</td>
</tr>
<tr>
<td>32ᵇ</td>
<td>Toluene</td>
<td>14 ns; 36 ns</td>
<td>2 ns²; 274 ns; 5.21 µs</td>
</tr>
</tbody>
</table>

*Table 19 Excited state lifetimes obtained by the interpolation of the transient decays for compound 37-Mes and 32.⁴ Sample excited with a photodiode emitting at 320 nm, emission measured at the emission maxima. ⁵ Sample excited with a laser diode emitting at 337 nm, more details about the measurement are contained in the work published by Monkman ad co-workers.⁸⁴ ⁶ Values estimated by time-resolved photoluminescence spectra*

In both solvents, a satisfactory interpolation of the transient decay measured in the presence of air was obtained with a biexponential function. This estimation revealed the coexistence of two different processes characterized by two different lifetimes, one in the nanosecond and one in the tens of nanoseconds range. The longer component constituted the main portion of the transient decays and was assigned to the prompt fluorescence emission of 37-Mes from ¹CT. This suggested that upon irradiation, the generated exciton could undergo electron transfer and directly generate ³CT, in analogy to what had been observed by Monkman and co-workers for compound 32.³⁸⁴ The faster component, which only constituted a small part of the transient, might be generated by the radiative relaxation of a locally-excited
state. As previously mentioned, the main fluorescence emission recorded for the aerated toluene solution is partially superimposed with a much weaker emission resembling the isolated acceptor moiety. However, we could not prove that the emission peak measured in THF is the additive product of two different radiative decays, which leaves the assignment of the fast decay component, under this condition, open.

In the absence of air, the transient decays are considerably longer and present two visibly distinct regimes that we both assigned to the radiative decay from $^1$CT. This designation was motivated by the fact that under these conditions, in both solvents, the emission profiles displayed only one peak which corresponded to the main peak observed in the presence of air. We also assumed that the locally-excited state’s emission would negligibly contribute to the transient decay considering the increase in the intensity of the CT-related emission.

The fast initial component of both decays, with an associated lifetime in the hundred of nanosecond range, was assigned to the early-mentioned prompt fluorescence emission from $^1$CT, which is populated directly upon photoexcitation. It must be noted that the lifetime of this component was one order of magnitude higher than the one observed in the presence of air. This difference was also attributed to the absence of oxygen in the solution. The biomolecular interaction with oxygen had been shown to quench fluorescence emissions to some extent, even though no triplet excited states are involved in the emissive process. The second portion of the transient decay, with a lifetime in the microsecond range, was not observed in the aerated sample and was assigned to the thermally activated delayed fluorescence from $^1$CT. As discussed for the emitters of class spiro-B, the emission associated with this long component originates from the same $^1$CT excited state of the prompt fluorescence; however, this state is populated via reverse intersystem crossing from the related $^3$CT rather than via direct charge separation of the exciton. The multi-stage process involved in this emission is what ultimately leads to its delayed nature, and the involvement of triplet excited states is what makes this emission susceptible to the presence of oxygen.

Fig. 166 Excited state decays measured for compound 37-Mes dissolved in toluene. The measurements were conducted under atmospheric condition (green dots) and in the absence of air under vacuum after thoroughly degassing the solution (blue dots). The sample was excited with a diode emitting at 320 nm. The inset shows a magnification of the two decays between 0 ns and 400 ns.
The photoluminescence quantum yield for the degassed toluene solution of compound 37-Mes corresponded to 15%. A direct comparison with compound 32 was not possible since a value for the photoluminescence quantum yield of the emitter under the same conditions has not been reported. This value is significantly higher than the one obtained for the compounds object of chapter 3, where the photoluminescence quantum yield could not be precisely measured due to its low magnitude. This result indicates that the molecular scaffold of compound 37-Mes more efficiently suppresses the relaxation via non-radiative processes compared to the one of the molecules of class spiro-B. However, the relatively low value for the photoluminescence quantum yield of compound 37-Mes indicates that non-radiative relaxation events still prevail in solution.

During the experimental work for this thesis, it was not possible to characterize the photophysical properties of polymeric thin films doped with the chromophore. As previously mentioned, these measurements are essential to obtain a complete assessment of the emitter’s photoluminescence performances, and they acquire added significance due to the aimed application of these emitters in OLEDs. From what was observed in chapter 3.4.2 and reported in the literature, we expect the inclusion of the emitter in the polymeric matrix to significantly affect the emitter’s photoluminescence quantum yield. The rigid environment should help inhibit molecular vibrations, therefore suppressing non-radiative deactivation pathways and increasing the emission efficiency.

In conclusion, the photophysical behavior of compound 37-Mes met our expectations, and the measured lifetimes of the excited state strongly resembled the one reported for 32. The most significant difference that could be noted between the two compounds concerned the emission profile. Specifically, the emission of compound 37-Mes was detected at a higher energy than the one of 32. This divergence is the product of the structural difference between the acceptor moiety of the two emitters, which altered the HOMO-LUMO energy difference of the chromophores. The results furnished by the analysis illustrated in this chapter strongly indicate that the fluorescence emission of compound 37-Mes indeed took place from a singlet excited state with a charge-transfer character. Additionally, it could be verified that, in the absence of oxygen, triplet excited states contribute to the same radiative decay leading to an increase of emission intensity. Therefore, we could confidently assume that part of the emission observed for compound 37-Mes occurs via TADF as observed for 32.

A more extensive study of the photophysical properties of this family of compounds assisted by computational calculations is needed to properly characterize the observed photophysical process. For instance, a temperature dependency study of the emission could yield more information regarding the energy of the excited states involved in the emission. It would also be adequate to exclude the involvement of triplet-triplet annihilation in the delayed emission by determining the relationship between the excitation and emission intensity. Nonetheless, with this brief investigation, the potential of this family of compounds as promising TADF emitters was confirmed. These initial results also motivate the synthesis of other derivatives of compound 37-R to evaluate the effect of different substituents at the boron center in the emission wavelength and the other photophysical properties.
5. TADF emitters as photocatalysts

5.1. Introduction

In chapter 3.4, it has been shown that the photoexcitation of compound 55 generates a triplet excited state with a remarkably longer lifetime compared to the other compounds of the same class reported in this work. This feature is what ultimately renders the luminescence of this compound extremely persistent but at the same time particularly prone to be quenched by oxygen. Luminescence quenching upon contact with air was observed in solution and even when the chromophore was embedded in polymeric thin films, which was another behavior observed exclusively for this specific emitter.

Material with a persistent luminescence that is highly sensitive towards oxygen can be applied in bioimaging. However, a long-lived excited state lifetime is a sought-after property also for molecules employed as photoredox catalysts and photosensitizers. The longer the photoredox catalyst persists in its excited state, the higher are the probability for the photoinduced electron transfer (PET) or energy transfer to a reagent to occur, which enhances the efficiency of the photocatalyst itself.

An accessible excited state with a triplet multiplicity is an essential requirement for photosensitizers. Only these excited states can yield an efficient energy transfer to the oxygen in its triplet ground state and generate the more reactive singlet oxygen. Nonetheless, the multiplicity of the excited state could also be relevant for photoredox catalysts. The lower energy of a triplet excited state compared to the one of the respective singlet excited states implies lower oxidizing or reducing capabilities for the catalyst. However, employing a photoredox catalyst whose activity is based on triplet excited states, showed to be beneficial for reactions in which back electron transfer negatively affects their efficiency. The excited state generated via PET from a photoredox catalyst in the triplet state is more likely to generate free ions instead of back electron transfer, therefore, promoting the desired transformation.

In light of these considerations, we decided to analyze whether the interaction between the triplet excited state of compound 55 and oxygen could be turned to our advantage by employing this compound as a photosensitizer. We also performed additional tests to evaluate if the long-lived excited state could also use to catalyze transformations that proceed via PET. The concept of taking advantage of the long-lived excited state of organic TADF emitters for the photocatalysis of chemical reactions has already been explored in some studies. In these examples, the chromophore had been used either alone or coupled to a metal center. The most frequently encountered emitter in this context is 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (1). This chromophore had been successfully used as a catalyst in many photocatalyzed transformations either alone or combined with nickel or palladium complexes in a dual photoredox systems. Particularly relevant in this context is the recent work of Milsmann and co-workers who recently reported the synthesis of a TADF emitter based on a complex of the early transition metals zirconium. Not only the complex proved to be an efficient TADF emitter but it also showed activity as a photosensitizer as well as a photoredox catalyst.

One of the factors that can be used to forecast a photocatalyst’s efficiency is its photoluminescence quantum yield since non-radiative relaxation of the excited state would compete with the energy- or electron-transfer processes. It follows that chromophores with a higher quantum yield are more likely to
act as efficient photoredox catalysts or photosensitizers. Regarding this aspect, the compounds belonging to class-B displayed, unfortunately, a particularly low quantum yield in solution even in the absence of air. Therefore, we expected that the competition of the non-radiative relaxation might hinder or limit their application as photocatalysts or photosensitizer. For this reason, we decided to perform the same tests using compound 37-Mes, which displayed a shorter excited state lifetime compared to compound 55 but a higher quantum yield in solution.

The two chromophores were tested as catalysts in the reactions listed in Fig. 167. The first two transformations imply the generation of singlet oxygen and were used to test the performances of the chromophores as photosensitizers. Conversely, the last three reactions are initialized by the electron transfer between the catalyst in its excited state and the reagents; therefore, they were chosen to test the performances of the chromophores as photoredox catalysts. For all the described experiments, a set of two UV lamps emitting in the range between 315 and 400 nm was employed as the light source. The procedure and additional conditions for the single transformations are described in the following sub-chapters.

1.  

\[
\begin{align*}
\text{phenyl sulfide} & \xrightarrow{\text{O}_2} \text{phenyl sulfone}
\end{align*}
\]

2.  

\[
\begin{align*}
\text{2-hydroxy-3-hydroxydihydroacenaphthenone} & \xrightarrow{\text{O}_2} \text{2,3-dihydroxydihydroacenaphthenone}
\end{align*}
\]

3.  

\[
\begin{align*}
\text{Ph} & \xrightarrow{\text{Ph}} \text{Ph}
\end{align*}
\]

4.  

\[
\begin{align*}
\text{1,2,3,4-tetrahydroisoquinoline} & \xrightarrow{\text{O}Ac} \text{1,2,3,4-tetrahydroisoquinoline}
\end{align*}
\]

5.  

\[
\begin{align*}
\text{2,3-dimethyl-1,3-dioxolane} & \xrightarrow{\text{O}Ac} \text{2,3-dimethyl-1,3-dioxolane}
\end{align*}
\]

*Fig. 167 Reactions used to test the performances of compounds 55 and 37-Mes as oxygen sensitizers (reactions 1 and 2) and as photoredox catalysts (reactions 3, 4 and 5).*
5.2. 55 and 37-Mes as photosensitizers

5.2.1. Singlet oxygen and its generation

Dioxygen is the most abundant paramagnetic compound in our environment. The ground state of the molecule, denoted \( ^3\Sigma_g^- \), is characterized by two unpaired electrons with the same spin orientation found in the two degenerate \( \pi^+ \) orbitals and, therefore, has a triplet multiplicity. Fundamental for the reactivity that characterizes the oxygen molecule are its two low-lying singlet excited states which differ only by the electronic configuration of the \( \pi^+ \) orbitals. These two orbitals denoted \( ^1\Delta_g \) and \( ^1\Sigma_g^+ \) are 22.5 kcal mol\(^{-1}\) and 31.5 kcal mol\(^{-1}\) above the triplet state, respectively. The transition from the \( ^1\Sigma_g^+ \) to the \( ^1\Delta_g \) state is spin allowed and therefore fast, rendering negligible the role of \( ^1\Sigma_g^+ \) in chemical transformations. Conversely, the transition from the \( ^1\Delta_g \) to the \( ^3\Sigma_g^- \) state is spin forbidden, thus oxygen in the \( ^1\Delta_g \) state (referred as singlet oxygen or \(^1\)O\(_2\) from now on) is a relatively long-lived species which is more likely to participate in chemical transformations.

Possibly, the first reported use of singlet oxygen in chemical transformations is contained in the work of Fritzsche published in 1867. He observed that naphthacene reacted in the presence of light and oxygen and that the product could be converted back to the starting material upon heating. At the time of the observation, however, the nature of the reaction product, as well as the active oxygen species, was not known. The first clues about the formation of a reactive \( ^1\)O\(_2\) species were obtained only later thanks to the pioneering experiments of Kautsky and de Bruijn at the University of Heidelberg in 1931. The research on the reactions promoted by singlet oxygen and their mechanism flourished in the last part of the 20th century whereas, in the last two decades, the efforts were focused in enhancing the regio- and stereo-selectivity of some of these transformations and in the application of the developed methods in various contexts.

To cite only a few examples, reactions promoted by singlet oxygen were incorporated in complex sequences of total synthesis, used in the cycloaddition of amines to fullerenes, and implemented in flow chemistry setups. Nowadays, singlet oxygen doesn’t only find applications in fine chemical synthesis but also in wastewater treatment, photodynamic therapy, blood sterilization, sunlight-activated herbicides and insecticides, as well as photodynamic cancer therapy. It also plays an essential role in the photodegradation of polymers, DNA damage, and other biochemical reactions.

Singlet oxygen can be produced chemically via various transformations, e.g., the reaction between hydrogen peroxide and sodium hypochlorite, the reaction between ozone and phosphite esters or triethylsilane, and the Haber-Weiss reaction. Alternatively, singlet oxygen can also be generated by direct photoirradiation at a wavelength of 765 nm (although the efficiency of this process is low due to the low molecular absorbance) or also via more specialized physical methods as electric or microwave discharge. Nonetheless, the most used and practical method for the generation of singlet oxygen remains the energy transfer between molecular oxygen and a chromophore in its excited triplet state. When chromophores are used in this process, they are also referred to as photosensitizers.

A wide variety of compounds can be used for the generation of singlet oxygen via this energy transfer mechanism. Among them are organic dyes, porphyrins, phthalocyanines, semiconductors, and transition
metal complexes. Independently from the kind of compound used, what ultimately determines the efficiency of a photosensitizer are its photophysical properties and in particular, the energy of its lowest excited triplet state. The characteristics that an ideal photosensitizer should possess are a high absorption coefficient at the wavelength of excitation, a triplet state of appropriate energy (\( E_T \geq 22.6 \text{ kJ mol}^{-1} \)), a high quantum yield of the triplet state (\( \phi_T > 0.4 \)), long triplet state lifetimes (\( \tau_T > 1 \mu\text{s} \)) and high photostability.\(^{396}\)

The performance of a photosensitizer can be assessed by exciting the chromophore in air-equilibrated solutions and measuring the intensity of the emission at 1270 nm, which is highly specific for the transition from \( ^1\Delta_g \) to \( ^3\Sigma_g^- \).\(^{412}\) Alternatively, the photosensitizer can be employed in a suitable reaction, and its sensitizing performance quantifies via the determination of the reaction rate.

The reactions in which singlet oxygen takes part can be mainly divided into two categories: the oxidation of heteroatoms and the reactions with unsaturated bonds. In the kind of reactions, the most prominent examples are ene reactions or [2+2] and [2+4], cycloadditions. The following chapter will illustrate the use of compounds 55 and 37-Mes as photosensitizers in two well-known reactions representing each one of the two categories, the photooxidation of thioanisole and the photooxidation of 1,5-dihydroxynaphthalene. These two test reactions are not only of preparative interest but have also been used to assess photosensitizers’ performances in the literature.

5.2.2. Oxidation of thioanisole

The first thoroughly studied photooxidation of sulfides via singlet oxygen was reported by Gollnick and Schenck, who investigated this transformation together with other fundamental photosensitized reactions.\(^{413}\) Since this early report, the reaction has been extensively studied, and recent investigations have focused on identifying the reactive intermediates. Among the most recent developments is also worth mentioning the combination of this transformation with double bond migration and the use of heterogeneous sensitizers such as polymers or zeolites.\(^{400, 414-417}\)

The oxidation of thioanisole to methyl phenyl sulfoxide, in particular, is a reaction that has often been used to test the performances of both photosensitizers and photoredox catalysts.\(^{418-421}\) It must be noted, in fact, that this reaction can show a dichotomy regarding its mechanism, as it had also been reported for the photo oxygenation of alkenes.\(^{422}\) In some instances, discerning between the two mechanisms is further complicated because one chromophore does not necessarily promote only one of the two different courses. For instance, 9,10-dicyanoanthracene (DCA), acts as both a photosensitizer and as a photoredox catalyst leading to the oxidized product via singlet oxygen production but also PET.\(^{423, 424}\) The investigation of the mechanism investigation can be made more complex by the fact that different photoredox catalysts can even promote different mechanisms which remain nonetheless based on PET.\(^{425}\)

In contrast to the photosensitized process, the mechanism of photooxidation of sulfides via PET had been less investigated, but it could be demonstrated that the two mechanisms involve the formation of different intermediates and are therefore markedly distinct. Investigations of the mechanism based on PET using N-methylquinolinium (NMQ') and DCA, strongly indicates a thiaoxirane as the possible intermediate (Fig. 168).\(^{426}\) In another study that examined the photoredox catalyst's reactivity of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP+BF4−), it was shown that the mechanism must be different since the catalyst is unable to generate \( \text{O}_2^* \). In this second case, the authors postulated the formation of a complex between molecular oxygen and the sulfite radical cation.\(^{423, 424}\) Generally speaking, the reaction
based on PET is less efficient than the one based on singlet oxygen but has a broader scope and insensitivity to substrate structure and reaction conditions making this method a valid alternative for the oxidation of sulfides that cannot be reacted with singlet oxygen.

\[
\begin{align*}
\text{hv} & \quad \text{Cat}^+ \\
\text{Cat} & \quad \text{R}_1^\text{R}_2^\text{S} \\
\text{O}_2^- & \quad \text{Cat} \\
\text{R}_1^\text{R}_2^\text{S}^{++} & \quad \text{R}_1^\text{R}_2^\text{S} \\
& \quad \text{R}_2^\text{S} \\
& \quad \text{R}_1^\text{R}_2^\text{S}^{++} \\
\end{align*}
\]

\[R_1^R_2= \text{butyl}\]
\[\text{or}\]
\[R_1 = \text{methyl, } R_2^= \text{phenyl}\]

*Fig. 168 Reaction mechanism for the photooxidation of dibuthylsulfide or thioanisole via photoinduced electron transfer reported by Baciocchi and co-workers.*

In the photosensitized oxidation of thioanisole, the first step of the mechanism corresponds to the formation of a persulfoxide intermediate (Fig. 169). After this initial step, the course of the mechanism is determined by the solvent employed in the reaction, which has, therefore, a significant influence on the reaction rate and the product distribution. In aprotic solvents, a hydroperoxysulfonium ylide is formed via α-hydrogen extraction and can react in two different ways.

It can either interact with another molecule of sulfide, generating two molecules of sulfoxide, or rearrange to give a molecule of sulfone. Conversely, in protic solvents, the persulfoxide intermediate is stabilized via the formation of hydrogen bonds with the reaction medium, and formation of the hydroperoxysulfonium ylide is not observed. The reaction between the stabilized intermediate with another molecule of sulfide finally yields two molecules of sulfoxide.

Additionally, it must be noted that the choice of the solvent can also influence the reaction in an indirect manner by affecting the concentration of ground state and singlet state oxygen in the reaction medium. Oxygen displays different solubility depending on the solvent, which affects its concentration in the reaction mixture. But more importantly, it must also be considered that the nature of the solvent influences the lifetime of singlet oxygen which ultimately affects its availability in the reaction medium. As reported in the work of Albini and co-workers, the extent of sulfoxidation in the presence of DCA increases by a factor of three changing the solvent from DCE to CH$_3$CN or CH$_3$OH due to the more efficient conversion of the persulfoxide intermediate to the sulfoxide. However, the increase of the reaction rate is attenuated with respect to the expected behavior. The damped increase was ultimately attributed to the shorter lifetime of $^1$O$_2$ in MeOH (ca. 50 ms for CH$_3$CN and DCE, 7 ms for CH$_3$OH). The choice of the reaction solvent is therefore subject to a compromise between the stabilization of the reaction intermediate and the availability of singlet oxygen.
Among all the numerous examples of sensitizers that had been tested in this reaction, also the well-known class of organoboron compounds, boron-dipyrromethenes (BODIPYS), was successfully employed. Such compounds have the advantage of being highly photostable and of displaying high quantum yields in solution; however, most of the compounds belonging to this class do not normally produce triplet excited states upon photoexcitation. A successful strategy to promote the population of excited triplet states in these family of chromophores was found to be the functionalization of the molecular backbone, either with heavy halogen atoms or by its connection to a transition metal center. Thanks to these modifications also these emitters could be turned into efficient photosensitizers for the generation of singlet oxygen.\textsuperscript{194, 421, 429} Compounds belonging to this modified subclass of BODIPYs chromophores were not only applied in photooxidation reaction, including the conversion of sulfides to sulfoxides, but also showed possible application in photodynamic therapy.\textsuperscript{430-433}

5.2.2.1. \textit{Kinetic experiments}

The kinetic studies regarding the oxidation of thioanisole were conducted using either compound 55 or 37-Mes as photosensitizer and a binary mixture of DCM and methanol as the solvent. The reactions were run in a closed vessel which size was properly chosen to ensure the presence of a large excess of oxygen with respect to thioanisole. As control experiments, three different reactions had been parallelly run: a reaction without any photocatalyst, a reaction in which compound 83 was used as the photocatalyst, and, finally, a reaction in a covered vessel. The purpose of the last control experiment was to hinder the interaction with the light source while allowing the reaction mixture to be at the same temperature as the other samples. Using compound 83 allowed us to test, under certain approximations, whether singlet oxygen could also be generated by a locally-excited state, centered on the acceptor fragment (see chapter 3.4.1.1) or if the interaction between oxygen and the charge-transfer excited state of compound 55 was essential for the photooxidation to take place.

The reaction progress could be monitored either via NMR spectroscopy or GC-MS. Using NMR, the reaction progresses could be precisely quantified by integrating the signal assigned to the methyl group of thioanisole and the other reaction products. However, we found the analysis via GC-MS to be more suited to the purpose. The analytical technique required the least amount of reaction mixture, and the reaction’s progress could be quantified with a higher frequency. The species’ concentration in the mixture
was then calculated by multiplying the initial concentration of thioanisole for the relative area of the chromatographic peaks associated with the different components. A method that would be more suitable to properly quantify the reaction progress would imply using a suitable internal standard and calibration curves for the detected species. However, due to the explorative character of this study, we did not mean to gain precise insights into the reaction kinetic but rather to provide a general picture of the reaction’s outcome.

In all the experiments, the only species that could be detected were thioanisole and the mono-oxidation product methyl phenyl sulfoxide. At the end of the reaction catalyzed with compound 55, traces of methyl phenyl sulfone were also detected, but they amounted to less than 2% of the reaction mixture. The evolution with time of the methyl phenyl sulfoxide concentration for the catalyzed reactions is reported in Fig. 170. For both catalysts, the reagent’s concentration linearly decreased as a function of time, and accordingly, the product’s concentration showed a linear increase. This observation implies that the reaction follows in both cases a pseudo-zero-order kinetic. The calculated kinetic constants are $1.58 \times 10^{-5} \text{molL}^{-1}\text{s}^{-1}$ and $1.7 \times 10^{-6} \text{molL}^{-1}\text{s}^{-1}$ for the reaction catalyzed with compound 55 and compound 37-Mes, respectively.

![Fig. 170 Evolution of the concentration of methyl phenyl sulfoxide with time in the photooxidation reaction catalyzed by compound 37-Mes (blue dots) and 55 (red dots). The dashed lines correspond to the linear fit of the reported data for each catalyst.](image)

In this first comparison, compound 55 displayed superior photosensitizing performances compared to 37-Mes. The low photoluminescence quantum yield of compound 55 surely limits its activity; however, the longer lifetime for the triplet excited state could evidently compensate this disadvantage and even lead to a better performance than the one observed for compound 37-Mes. In the absence of air, the excited state lifetime associated with the delayed component of compound 55 (97.9 μs) is remarkably longer compared to the same lifetime recorded for compound 37-Mes (7.8 μs), see chapter 3.4.1.2.2 and 4.3.2. This difference implies that for the former compound, the triplet excited state persists for a longer time before undergoing conversion to the singlet excited state or lose its energy through non-radiative processes. A longer lifetime for the triplet excited state corresponds to an increase in the probability of
the bimolecular collision between the oxygen molecule and the catalyst in its excited state, which ultimately corresponds to a greater efficiency of the energy transfer process.

In the control reactions, performed in the absence of light or without any photocatalyst, only traces of phenyl methyl sulfoxide were detected. This outcome confirmed that the two sensitizers indeed promoted the observed reaction. Surprisingly, in the reaction where compound 83 had been employed as the sensitizer, a small conversion of approximately 12% of thioanisole to the sulfoxide was observed. As a comparison, the reaction catalyzed by compound 55 reached complete conversion of the starting material during the same time. This result highlighted the superior sensitizing performance of compound 55 and therefore the benefit of the donor-spiro-acceptor architecture, but it also showed that compound 83 could act as a photosensitizer as well, albeit with far worse performances. The fact that also the photoexcitation of compound 83 could lead to the generation of singlet oxygen may be connected to the broad emission band observed in the emission spectra of this chromophore when the wavelength for the excitation of the sample corresponded to 300 nm. This may suggest that also for this compound the formation of a charge transfer excited state and relatively long-lived triplet excited states may be possible however, any speculation is unfounded since the photophysical properties of this emitter were not thoroughly investigated.

5.2.2.2. Self-oxidation of compound 55

When the reaction catalyzed with compound 55 was monitored via 1H NMR spectroscopy, we could observe that both the signals assigned to thioanisole and the signals of the catalyst itself changed. Specifically, the intensity of some of the signals assigned to the catalyst diminished over time while the intensity of a new set of signals gradually increased. After the reaction approached completion, however, the newly observed signals slowly faded while the one characteristic of the catalyst could be detected again.

These initial observations suggested that not only thioanisole underwent a transformation but also the catalyst itself and that the reaction involving compound 55 displayed a reversible nature. Since the catalyst incorporated a sulfide bridge in its structure, we hypothesize that the sulfur heteroatom of compound 55 could also be oxidized to the corresponding sulfoxide or sulfone under the reaction conditions. In analogy with the above-discussed mechanism, we could postulate that the oxidation of the photosensitizer could proceed either via direct reaction with the generated singlet oxygen or via oxygen extraction from a persulfoxide intermediate. The observed reversibility would then suggest that the oxidized catalyst could transfer the oxygen found at the sulfur atom to another species, such as thioanisole. It must be mentioned that, in the experiments monitored via NMR, the amount of oxygen was limited due to the small volume of the reaction vessel. Therefore, it must be considered that the oxidation reaction's reversibility might only be observed under a deficiency of oxygen or in excess of the oxygen-acceptor.

To gather more insights into the catalyst transformation and verify our hypotheses, we performed a modified version of the previously illustrated photooxidation. The reaction was carried using the same solvent mixture but with a higher catalyst concentration and without adding thioanisole to the reaction mixture. The solution was initially irradiated under air for 18 h after which only partial conversion of 55 to the same unknown species could be observed. The reaction mixture was then further irradiated, and, to accelerate the transformation, pure oxygen was used instead of air. After 8 h under these conditions, the starting material was completely converted. TLC analysis showed only one spot, which interestingly
lost the characteristic orange fluorescence of the starting material and displayed a blue fluorescence instead. Surprisingly, the interpretation of the NMR spectrum of the new material revealed the presence of two different sets of signals which would indicate the presence of two different species.

Separation of the two compounds could not be obtained either via column chromatography or crystallization; however, it must be mentioned that a slight change of the relative amount of the two compounds in the mixture was observed after the attempted chromatographic separation. Further insights about the obtained material could be gained from the x-ray diffraction analysis of crystals grown from one of the fractions delivered by the chromatographic separation. The obtained solid-state structure is reported in Fig. 171 and corresponds to the mono-oxidation product at the sulfur atom of compound 55. The two sets of signals could then be attributed to the two different diastereomers that the oxidation process can produce. The two isomers differ in the relative position of the oxygen atom with respect to the nitrogen center of the acceptor fragment. The existence of two stable configurations is made possible by the fact that, for sulfoxides, the interconversion between the two conformations of the sulfur center occurs at a significant rate only at temperatures higher than 200°C. Additionally, the rigid molecular backbone based on the spiro architecture blocks the relative rotation of the two moieties hindering any other possible interconversion between the two isomers. In Fig. 171 is reported only one of the two isomers in which the oxygen and the nitrogen atoms are found on the same side of the molecular structure, but both diastereomers were observed in the obtained solid-state structure. Accordingly, NMR analysis of the measured crystal showed two sets of signals corresponding to the one observed in the NMR spectrum of the crude material, and the relative ratio between their intensity approximately corresponded to the ratio between the two isomers contained in the crystal structure.

![Figure 171](image1.png)

*Fig. 171 solid state and molecular structure of compound 77. Only one of the two detected diastereoisomers is reported.*

After the structure of the new species was defined, we proceeded to investigate the reversibility of the oxidation reaction and the possibility of transferring the oxygen atom to another substrate. However, it must be mentioned that the photo-promoted deoxygenation of sulfoxides had already been proved to be possible. In particular, Taylor, Unsworth, Rossi-Ashton, and co-workers provided in their works a detailed study of the reaction mechanism and its application in various syntheses procedures. To evaluate if compound 77 could be photoreduced to compound 55 and if the oxidized chromophore was
able to transfer its oxygen atom to another compound, we irradiated compound 77 in the presence of an excess of thioanisole under an inert atmosphere.

The above-mentioned reaction between compound 77 and thioanisole was monitored using NMR spectroscopy. In Fig. 172 are reported the NMR spectra of the reaction mixture analyzed at different irradiations times. As it can be seen, after 3.5 h of irradiation, the mixture of the two different diastereomers was fully converted to compound 55. The outcome of these measurements confirmed the reversibility of the oxidation reaction, but unfortunately, the presence of a large excess of thioanisole did not allow us to verify the production of methyl phenyl sulfoxide.

The elements collected with the reported experiments indicate that the mechanism of the photooxidation reaction performed using compound 55 as the photosensitizer may differ from the one illustrated at the beginning of this chapter. It is mandatory to consider that under the reaction conditions also the sensitizer itself could be oxidized and that such oxidation is reversible. Therefore, it cannot be excluded that the reaction may proceed via the oxygen transfer from the catalyst to thioanisole instead of the direct interaction between singlet oxygen and the thioether. It is also possible that, under the reaction conditions, the oxidation of compound 55 occurs mainly via the interaction with the persulfoxide.

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**Fig. 172** NMR monitoring of the reaction between compound 77 and excess thioanisole under the irradiation of UV light. Solvent employed: MeOD-d4-DCMe-d2 -. Spectrum 1: reaction mixture before irradiation. Spectrum 2: reaction mixture after 3.5 h of irradiation. Spectrum 3: pure 55 dissolved in the same solvent system. The area of the spectra in which the signals of thioanisole can be found is marked with the symbol *. 
derivative of thioanisole. The photosensitizer could then be regenerated via the transfer of the oxygen atom to a second molecule of thioanisole (Fig. 173).

The photosensitizer could then be regenerated via the transfer of the oxygen atom to a second molecule of thioanisole. The participation of compound 77 in the reaction mechanism could also help to explain why the reaction kinetic follows a pseudo zero order. However, it would still be unclear why the same kind of trend should be observed for the reaction where compound 37-Mes is used as the sensitizer. An analogous oxygen-transfer mechanism involving compound 37-Mes is unlikely to happen since a photooxidation reaction that could lead to the oxidation of the nitrogen atom of its donor moiety has yet to be reported.

An additional key point that must also be considered is that the oxidation of the donor fragment has a major impact on the photophysical properties of compound 77. As reported in greater detail in chapter 5.4, the oxidation of the donor moiety of compound 55 clearly impairs the donor capability of the fragments. Consequently, the formation of a charge-transfer excited state and the related TADF emission are also inhibited. Therefore, it must be clarified if and to which extent the generation of singlet oxygen can also be performed by compound 77. Due to the high number of open questions about the reaction catalyzed with compound 55, we were unable to make any precise assumption regarding the mechanism followed by this specific photooxidation. Nonetheless, the fact that, despite the oxidation of the sensitizer, the photooxidation promoted by compound 55 could still reach completion and at an even faster rate than the reaction catalyzed with 37-Mes motivates the investigation of the reaction mechanism.

5.2.3. Oxidation of 1,5-dihydroxynaphthalene

The photooxidation of 1,3-dihydroxynaphthalene (DHN) is another reaction that is often used to assess the performances of photosensitizers. The reaction mechanism is reported in Fig. 174 and proceeds through the formation of an endo-peroxide via the 1,4 cycloaddition of singlet oxygen to the aromatic ring. The endo-peroxide subsequently undergoes hydrolysis yielding the allylic hydroperoxide. As reported by Oliveros and co-workers, the observation of a deuterium isotope effect supports the involvement of acid catalysis in this initial part of the mechanism. After the oxidation of the hydroperoxide via either homolytic or heterolytic cleavage, the reaction product, juglone, is finally obtained. In analogy to what had been shown for thioanisole, this reaction can also be catalyzed via photoredox catalysts.
Fig. 174 Schematic representation of the reaction mechanism of the photosensitized oxidation of 1,5-dihydroxynaphthalene.

In the previously reported investigations, the reaction progress had been determined by UV-vis absorption spectroscopy which represents an even faster analytical method compared to GC-MS and requires even lower amounts of analytes. In our case, the setup used for the initial screening consisted of two parallel reactions, one monitored via UV/vis absorption spectroscopy and the other via NMR. In the two reactions, only compound 55 was tested as the sensitizer, and a mixture of methanol and DCM in ratio 9/1 was used as the reaction solvent. The only difference between the two experiments consisted in the DHN and catalyst concentrations which had to be adjusted according to the detection limit of the different analytical techniques used. Nonetheless, the relative ratio between the species was kept constant. In this initial screening, we detected discrepancies between the results obtained with the two analytical techniques. Specifically, in the reaction monitored via UV/vis absorption spectroscopy, the collected spectra showed changes similar to the one reported in the literature, but the analysis via NMR spectroscopy did not register any conversion of the starting material. One of the problems that could have affected this comparison is the different concentrations of the species in solution; however, even extending the reaction time of the experiment monitored via NMR did not lead to any detectable conversion. It must also be noted that, despite resembling the one reported in the literature, the evolution of the UV-vis absorption spectrum did not exactly replicate the one previously described.

In the second set of experiments, we decided to monitor the reaction progress exclusively via NMR spectroscopy. We consider this technique to be more suitable for our purpose than UV-Vis spectroscopy since it could furnish a clearer picture of the reaction progresses in case different species formed. Additionally, in this second screening, also the photosensitizing performance of compound 37-Mes was evaluated. Due to the low solubility of 37-Mes in methanol, equal amounts of DCM and methanol were used in the solvent mixture. Under these new conditions, photooxidation of DHN was observed with both photocatalysts but also in the control experiment performed without photosensitizer. The conversion observed in the control experiment without a catalyst was not remarkably inferior to the catalyzed reaction, which highlighted the presence of a problem in the experimental setup.

The discrepancies between the results delivered by the two employed analytic techniques and the surprising outcome of the control experiment highlighted the need to deeply analyze every aspect of the experimental setup and apport suitable changes. Therefore, due to the explorative nature of this study, we decided to favor the investigation of the previously reported photosensitized oxidation and suspend the experiments that involved the photooxidation of DHN.
5.3. 55 and 37-Mes as photoredox catalysts

5.3.1. Introduction to photoredox catalysis

The fundamental difference between photoredox catalyzed reactions and the photosensitized transformations concerns the nature of the interaction between the catalyst and the substrates. A photoredox catalyzed process is based on the net exchange of electrons between one of the reactants and the catalyst in its excited state. This type of catalyzed reaction strongly differs from the photosensitized transformations since \( \text{O}_2 \) is generated via energy transfer, and no net exchange of electrons is observed. Additionally, photoredox processes do not rely on the use of oxygen and cover a much wider number of transformations. Furthermore, the possibility of creating dual-catalytic systems additionally increases the number of transformations that can be achieved thanks to this kind of catalysis. In these tandem systems, the photoredox catalytic cycle is coupled with other catalysts, e.g., Lewis and Brønsted acids, organocatalysts, enzymes, or transition metal complexes. Lastly, it must be noted that, despite the high energy associated with excited states, it had been shown that even enantioselective photoredox-catalyzed transformations could be achieved by a careful design of the catalyst or by using a chiral co-catalyst.

To gain orientation in the vast number of transformations that belong to this category, a photoredox catalyzed reaction is typically categorized according to two criteria. The first one concerns the direction of the electron exchange taking part in the first step of the mechanism. A reaction is then classified as either a photooxidative or a photoreductive process, whether the first stage of the mechanism involves the oxidation or the reduction of the photocatalyst, respectively. The second criterion regards the net redox balance of the reaction. Therefore a photoredox reaction can be classified as a net oxidative, net reductive, or redox neutral transformation depending on the oxidation state of reagents and products.

Due to the great variety of photoredox transformations that have been reported and due to the explorative nature of this study, we decided to test the two chromophores 55 and 37-Mes in reactions that made use of readily available starting materials. The two selected transformations are the cyclization of geraniol or geraniol acetate and the [3+2] cycloaddition of acrylonitrile and stilbene oxide. These two reactions do not represent, by any means, the wide variety of reported photocatalyzed transformations since they are both photo-oxidative, redox-neutral reactions. It will be the task of future studies to expand the tested transformations considering the result of this preliminary work.
5.3.2. Oxidative cyclization of geraniol and geraniol acetate

The photocatalyzed cyclization of a polyene is a remarkable reaction that enabled the synthesis of complex polycyclic structures in one single step. This photoredox reaction efficiently mimics the activity of the enzymes class of terpene cyclases, and it is highly relevant from a synthetic point of view. A significant number of isolated natural products are, in fact, constituted by a fused polycyclic backbone, as is the case for all the formal derivatives of sterol.\textsuperscript{446, 447} Additionally, this reaction had also been applied to the total synthesis of complex natural products, e.g., in the synthesis of $(\pm)$-Stypoldione reported by Demuth and Xing.\textsuperscript{448} The first stage of the mechanism includes the oxidation of the double bond at the gamma position of the polyene starting material and the formation of a radical cation. The parent radical cation is then selectively trapped by a nucleophile at the anti-Markovnikov position generating the radical that initiates the cyclization. The termination of the cyclization proceeds either via the reduction of the radical and its successive protonation or via reaction of the radical with an atom of hydrogen (Fig. 175).

![Fig. 175 Representation of the mechanism for the photoinduced polyalkene cyclizations of all-trans-geranylgeraniol reported by Demuth and co-workers.\textsuperscript{448} The reaction is catalyzed by $1,4$-dicyano-$2,3,5,6$-tetramethylbenzene (DCTMB) and $1,1$'-biphenyl is used as the electron acceptor.](image)

In addition to the photoredox catalyst, electron acceptors such as biphenyl are generally employed to further promote the reaction. One competing photopromoted side reaction is the isomerization of the substrate double bonds. This transformation is favored if the generation of the initial radical cation cannot take place. The reaction outcome can be influenced by not including a nucleophile in the reaction mixture or by varying the substituents present on the polyene backbone.\textsuperscript{450, 451} Thanks to the high face selectivity of this reaction, products of complementary chiralities could be obtained and the presence of a single chiral auxiliary is required, e.g., ($\pm$) menthone as reported in the work of Demuth and Heinemann.\textsuperscript{452}

The initial generation of the radical cation represents a critical point in the mechanism of this reaction, and the polarity of the solvent strongly influences it. In more polar solvents, the Coulombic barrier that needs to be overcome to achieve the separation between the photoredox catalyst and the oxidized substrate is significantly lowered.\textsuperscript{453} For this reason, the use of neutral photoredox catalysts in apolar solvents does not always lead to the generation of the radical cation and back electron transfer is often favored under these conditions. On the other hand, polar solvents react much faster with radicals than low polarity solvents which limits the efficiency of the reaction. A method to hinder the back electron transfer process in apolar solvents is to use cationic photoredox catalysts.\textsuperscript{454} In this case, upon oxidation of the double bond, the Coulombic interaction between the neutral reduced catalyst and the radical cation is generally low enough to ensure the diffusion of the charged species and avoid the recombination.
In the context of this work, we tested compounds 55 and 37-Mes as photoredox catalysts for the simple cyclization of geraniol and its acetate derivative since it constituted a much simpler and readily available system compared to the more extended polyenes. For the cyclization of geraniol, we applied the conditions reported by Heinz and co-workers, who performed the photopromoted cyclization of the same substrate using 9,10-dicyanoanthracene as the photoredox catalyst. The reported reaction was performed in dichloromethane and without the presence of a nucleophile to trap the initial radical cation (Fig. 176a). The cyclization of geranyl acetate was performed according to the conditions reported by Demuth and co-workers. (Fig. 176b) The reactions were monitored via NMR and performed under inert atmosphere to avoid the interference with oxygen.

For both substrates, the reactions had been performed under several different conditions. Increasing amounts of chromophore and co-sensitizer were used, and the irradiation time was extended up to 3 days. Despite the wide range of reaction conditions that had been tested, however, no conversion of the starting material was detected. Since our experimental setup did not correspond precisely to the one reported in the works taken as a reference, we additionally performed the cyclization of geraniol with 9,10-dicyanoanthracene to verify that conversion of the starting material could also be obtained using our experimental configuration. Using the reported photoredox catalyst, conversion of geraniol could be indeed detected, indicating that the absence of reactivity was not connected to the experimental setup. In the early works of Demuth and co-workers, it had been highlighted how conducting the reaction in a micellar medium could help promote the formation of the radical cation and therefore increase the efficiency of the reaction. However, this last strategy was not examined since it would have complicated the reaction monitoring and was shown to hamper the eventual isolation of the desired product.

5.3.3. Oxidative [3+2] cycloaddition reaction between acrylonitrile and stilbene oxide

the performances of 55 and 37-Mes as photoredox catalysts were also tested in a second reaction, namely, the photo-promoted [3+2] cycloaddition of stilbene oxide to acrylonitrile, firstly reported by Albini and Arnold. Analogously to the reaction illustrated in the previous chapter, this transformation is also a photooxidative process. However, the initial photooxidation does not involve the double bond of acrylonitrile but, instead, the epoxide ring of stilbene oxide. As schematized in Fig. 177, in the first step of the mechanism, the interaction between the excited photoredox catalyst and stilbene oxide generates a stilbene oxide radical cation, which, after rupture of the C-C bond, yields a carbonyl ylide lacking one
electron. The isomeric electron-deficient carbonyl ylides are not formed in equal amounts from the two isomers of stilbene oxide, and once they are generated, they preserve stereochemical integrity. These two characteristics are what ultimately causes this reaction to display a certain degree of stereoselectivity. The tetrahydrofuran end-product is generated in the last stage of the mechanism after back electron transfer from the catalyst, and cycloaddition of the obtained carbonyl ylide take place.

![Fig. 177 Reaction mechanism for the oxidative [3+2] cycloaddition reactions between acrylonitrile and epoxides reported by Albini and Arnold.](image)

To test the performances as photoredox catalyst of compounds 55 and 37-Mes we followed the reported protocol developed by Albini and Arnold. Acrylonitrile and trans-stilbene oxide were dissolved in toluene and irradiated for two days, under oxygen-free conditions, in the presence of either one of the chromophores. The reaction progress was qualitatively monitored via TLC-MS.

When 37-Mes was used as the photocatalyst, no appreciable consumption of stilbene oxide or the formation of new components in the reaction mixture were detected. The reaction monitoring did not even detect the production of deoxybenzoin, which is the byproduct generated by the direct photoexcitation of stilbene oxide.\(^{455}\) Conversely, in the reaction where 55 had been employed as the photocatalyst, small amounts of a new compound could be detected. Isolation of the newly observed band via column chromatography yielded a material that, according to the $^1$H-NMR analysis, was constituted by a mixture of different species. However, the analysis of the same mixture via mass-spectrometry suggested that all the component possessed the same mass and that the new species could be the addition products between acrylonitrile and the catalyst itself.

To gain more information about the newly observed product and obtain higher amounts of the material, the reaction was repeated under the same conditions except that stilbene oxide was excluded from the reaction mixture and that the amount of compound 55 was increased. The reaction indeed yielded the same mixture of compounds, and one of the components could be partially isolated via column chromatography. From this fraction, single crystals suitable for X-ray diffraction were obtained. The examination of the solid-state structure delivered by the X-ray diffraction analysis (Fig. 178) confirmed the above-mentioned hypothesis. It could be proven that at least one of the newly formed species,
compound 159, is the product of the combination between acrylonitrile and compound 55. The formation of the newly observed product most probability occurs via a photo-promoted [2+2]-cycloaddition reaction between the two species. In the case of compound 159, the double bond of the chromophore that took part in the cycloaddition reaction is specifically the ethylene bridge between the two external aromatic rings at the acceptor fragment. The reason behind the regioselectivity of the reaction is connected to the inhomogeneous aromaticity of the benzo[h]quinoline fragment. In analogy to what is observed in the molecule of anthracene, the central aromatic ring of this moiety should possess a weaker aromatic character. The lower stabilization of the central ring system is what rendered the central ethylene bridge more reactive and therefore subject to the cycloaddition reaction.

The [2+2] photocycloaddition reaction is a fundamental transformation that has been extensively used in organic synthesis, and it constitutes possibly the most used photochemical reaction. Its importance is even more highlighted by the fact that its thermally promoted version is forbidden by orbital symmetry. The reaction is based on the interaction between an excited olefine and a second unsaturated substrate in its ground state. It follows that a longer lifetime of the excited olefin is desired since it increases the probability of encounter between the two species. The long-lived excited triplet state observed for compound 55, together with the weak aromaticity of the central aromatic ring in the acceptor moiety, surely promoted the observed reactivity. Previously reported work had examined the 2+2 photocycloaddition of alkenes to phenanthrene, or the related polyaromatic hydrocarbons, pyrene or chrysene, but no analogous transformation involving the phenanthroline moiety had been described.

The other components of the mixture obtained by the reaction between 55 and acrylonitrile have not been further characterized. However, due to the high similarity between most of the NMR signals and the result of the mass-spectrometry analysis, we speculated that the other components could be isomers of compound 159 which differ from the position of the nitrile group. These additional isomers can be theoretically generated by cycloaddition reactions in which the two reaction partners are arranged with a different relative orientation than the one that led to compound 159. The production of more
stereoisomers is expected due to the absence of elements that could influence the relative arrangement of the two molecules and, consequently, the stereochemistry of the reaction. On the other hand, in agreement with what had been mentioned earlier, we expect the reaction to display a certain degree of chemoselectivity and always involve the same double bond at the acceptor fragment of compound 55. Further investigations are needed to confirm that the other products generated during the reaction indeed follow our hypothesis on the product distribution. It would also be relevant to investigate whether emitters with a different acceptor moiety would undergo the same reaction.
5.4. Photophysical properties of compounds 77 and 159

The two derivatives 77 and 159, obtained during the investigation illustrated in this chapter, were additionally characterized by mean of absorption and emission spectroscopy. Such analyses diverge from the initial goal of this section, but we considered them to be an additional opportunity to evaluate the effects of structural modification on the photophysical properties of this class of chromophores. We expected that the oxidation of the sulfur atom at the donor moiety would completely remove or at least strongly reduce the donor capabilities of the fragment and therefore lead to a significant worsening of the TADF performances of the emitter. The cycloaddition of acrylonitrile at the acceptor moiety of compound 55 clearly reduces the extension of the acceptor π system, but it does not compromise the accepting nature of the fragment. Therefore, for compound 159, we expected retention of TADF but a possible shift of the peaks in the absorption and emission spectra. As mentioned in chapter 3.4, the absorption spectra of this class of emitters are strongly influenced by the kind of donor moiety installed in the molecular scaffold. It was also shown that extension of the acceptor’s system leads to a reduction of the HOMO-LUMO energy difference and, therefore, to a red-shift of the emission peak. For this reason, we expected compound 159 to display a blue-shifted emission when compared to the one of compounds 55. To verify these hypotheses, the result of the measurements will be compared to the one of compound 51. A summary of the relevant measured parameters, which are discussed in this chapter, is summarized in Table 20.

5.4.1. Absorption spectra

As described in chapter 3.4, the absorption spectra of this family of compounds are strongly dominated by a transition localized on the acceptor moiety. As it can be seen in Fig. 179, also compounds 77 and 159 displayed absorption spectra that agree with this observation. In compound 77, the oxidation of the sulfur atom does not introduce changes at the acceptor fragment, and its absorption spectra show a similar absorption profile to the one obtained for compound 55. The most relevant difference between the two spectra is that the absorption onset is shifted of about 8 nm (508 cm⁻¹) and that the two peaks are less well resolved. Conversely, the cycloaddition reaction between acrylonitrile and compound 55 strongly modifies the π-system of the acceptor rendering it structurally more similar to a substituted 2-phenylpyridine fragment. This change is reflected in the considerable modification of the absorption spectra of compound 159 compared to the one of the parent compound 55. This derivative’s absorption profile resembles more the one of compound 51, which has indeed an acceptor bound to

the 2-phenylpyridine moiety. However, the two spectra do not superimpose, and in this case, the absorption spectrum of the derivative 159 displays a bathochromic shift of 9 nm (7.24·10² cm⁻¹) of its onset with respect to the one of compound 51.
5.4.2. Emission spectra and excited state lifetime

The photophysical properties of compounds 77 and 159 have been analyzed applying the same methods described earlier in this thesis. Their emission was recorded via fluorescence spectroscopy, and the excited state lifetimes were measured via TCSPC. Also, these measurements were conducted under ambient atmosphere and under vacuum to confirm the involvement of triplet excited states in the emission process and the possible observation of TADF.

Compared to the parent compound 55, the fluorescence emission of compound 77 is drastically shifted towards lower wavelengths, namely by 156 nm (6.41·10^4 cm⁻¹). As a consequence, the Stokes shift recorded for the chromophore, namely 2.45·10^3 cm⁻¹, is approximately one order of magnitude lower than the typical values observed for the other compounds of this class (Table 4, chapter 3.4.1). The emission peak of 77 also differs from the one of the previously measured chromophores in that it is slightly structured, with a shoulder before and after the main peak. The emission profile is also narrower than the one of its parent compounds, displaying a full width at half maximum of 3.34·10^3 cm⁻¹ against 3.89·10^3 cm⁻¹ measured for compound 55. The emission of 77 is therefore clearly different from the one of the other spiro compounds examined in this work, but it strongly resembles the one observed for compound 83. As it can be seen in Fig. 180a, both compounds have a similarly structured emission peak and a comparable Stokes shift, namely 1.14·10^3 and 2.45·10^3 for 83 and 77, respectively (the Stokes shifts were measured between the maximum of the emission spectrum and the closest peak to the absorption onset in the absorption spectrum).

The reported observations strongly suggest that the emission of 77 takes place from a locally-excited state, most likely centered on the acceptor moiety. The lack of an emission peak from a charge-transfer excited state was attributed to the diphenyl sulfoxide fragment’s poor donating capabilities, which, in turn, hampers the formation of an excited state with a charge-transfer character. We expected that the
inability to form a charge-transfer excited state would also induce the complete loss of TADF. This last hypothesis could be confirmed by the excited state lifetime measurements in the presence and absence of oxygen. Under both conditions, the decay of the excited state could be described with the same two decay components, both with an associated lifetime in the nanosecond time range, which excludes the involvement of triplet excited states in the emission process and, therefore, TADF.

In contrast to what had been seen for compound 77, the emission profile of compounds 159 resembled, in terms of shape and Stokes shift, the one recorded for the other chromophores of the class spiro-B. In terms of its energy, the emission of this new compound is closer to the emission observed for compound 51 than to the one of the parent compound 55 (Fig. 180b). Precisely, the energy difference between the emission maxima of compound 159 and the emission maxima of the two chromophores 51 and 55 measures 285 cm\(^{-1}\) and 1182 cm\(^{-1}\), respectively. The blue-shift observed in the emission of compound 159 with respect to the one of compound 55 is clearly connected to the dearomatization of the central ring at the acceptor fragment. As mentioned in chapter 3.4, reducing the extension of the acceptor π-system reduces the strength of the acceptor fragment and causes a blue shift in the emission maximum of the emitter. In terms of excited-state lifetime, compound 159 did not show the remarkably long decay of compound 55. Nonetheless, in the absence of oxygen, the transient decay showed a new delayed component with an associated lifetime of 3.24 μs which confirmed the emission via TADF for this emitter as well.

In summary, the results concerning the photophysical properties of compound 77 and 159 confirmed our hypothesis and supported the validity of the trends observed in chapter 3.4. The experiments performed in this chapter highlighted that compound 55 is not a suitable photoredox catalyst for photocycloaddition reaction due to the possibility of a reaction between the unsaturated substrate and compound 55 itself. Nonetheless, it could be shown that a [2+2]-cycloaddition reaction may be used to achieve an alternative modification of the molecular scaffold of compound 55, and it could be potentially applied to all the emitters that share the same acceptor fragment. This reaction constitutes an additional tool that can be used to influence the structural and photophysical properties of these emitters without totally inhibiting the TADF emission in analogy to the derivatization sequence of chapter 3.2.

Fig. 180 Normalized emission spectra of the newly obtained compounds 77 (a) and 159 (b) compared to the previously described chromophores 55 and 83 (a) or 55 and 51 (b).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption onset (nm)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; Emission (nm)</th>
<th>τ under air (fractional intensities)</th>
<th>τ under vacuum (fractional intensities)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>346</td>
<td>526</td>
<td>27.5 ns (64); 259 ns (36)</td>
<td>35 ns (16); 2.7 μs (84)</td>
</tr>
<tr>
<td>55</td>
<td>391</td>
<td>570</td>
<td>3.23 ns</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>97.9 μs</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>390</td>
<td>394</td>
<td>-</td>
<td>5.76 ns</td>
</tr>
<tr>
<td>77</td>
<td>400</td>
<td>414</td>
<td>0.78 ns (57); 4.26 ns (43)</td>
<td>0.81 ns (53); 5.01 ns (47)</td>
</tr>
<tr>
<td>159</td>
<td>356</td>
<td>534</td>
<td>16.9 ns (85); 119 ns (15)</td>
<td>39 ns (23); 3.24 μs (77)</td>
</tr>
</tbody>
</table>

Table 20 Characteristic photophysical properties of the newly obtained compounds 77 and 159 compared to the previously described chromophores 55 and 51.
6. Conclusions and Outlook

In the work dedicated to this thesis, was established the synthesis towards two new classes of boron-based donor-spiro-acceptor emitters, spiro-B and spiro-C, and the photophysical properties of the newly synthesized chromophores were investigated. The different molecular structure of the two families of compounds implied the development of two radically different synthesis approaches characterized by a different level of complexity. Chromophores of both classes displayed emission via TADF, which confirmed the relevance of the donor-spiro-acceptor architecture. Two chromophores, namely compound 55 and 37-Mes, were also tested as sensitizer and photoredox catalyst in a brief explorative study. The conducted experiments shown that both compounds could induce the formation of singlet oxygen upon irradiation, and their sensitizing ability was applied to the oxidation of thioanisole. Both chromophores, however, proved to be unable to promote the tested reactions based on PET. It was additionally proved that compound 55 can undergo modification of its structure under some of the tested reaction conditions. The sulfur atom of the chromophore could be oxidized under the condition of the photosensitized reaction generating compound 77 without, however, inhibiting the oxidation of thioanisole. Under irradiation, compound 55 also reacted with acrylonitrile generating a mixture of compounds in which 159 was detected.

In the following sections, is reported a more detailed summary of the adopted synthesis approaches and the measured photophysical properties for each class. Finally some possible strategies for the further development of the chromophores are suggested.

6.1. Emitters of the class spiro-B

The compounds belonging to the class spiro-B could be synthesized via the boron-destannylation protocol reported by Ingleson and co-workers or by the direct combination of a borylated phenyl pyridine derivative and a doubly metallated species. In both approaches, the acceptor and donor fragment of the final emitter could be selectively modified by simply substituting one of the two building blocks in the synthesis process, allowing straightforward and modular access to this class of compounds. The first synthesis strategy was the most suitable method to perform the synthesis of these emitters since it could consistently deliver the product in higher yields than the alternative method. However, the second approach had to be applied to the synthesis of compound 50, for which the tin-based protocol failed. Combining the two synthesis methods ultimately led to the synthesis of nine different emitters generated via the combination of three different donor fragments and five different acceptor fragments.

Additional chromophores belonging to this family of compounds were obtained by an alternative pathway that implied the derivatization of compound 56. This second strategy was not only designed to expand the compounds pallet but with the specific aim of generating chiral emitters with a stereocenter in correspondence of the central boron atom. This additional synthesis approach consisted of four main stages, namely, the mono bromination of the chromophore’s donor moiety, borylation of the halogenated position with a chiral boron residue, separation of the generated diastereomers, and substitution of the chiral fragment with an achiral substituent. In the borylation reaction, (+)-pinanediol was used as a chiral chelating substituent at the boron atom, yielding the couple of diastereomers En-64. It has been demonstrated that the two generated diastereomers could be separated via preparative HPLC on a
standard phase column. However, the separation could be performed only on a small sample, and the last step of the reaction sequence was performed with the mixture of the stereoisomers as a proof of concept. The reaction tested for the last step was a Suzuki-Miyaura coupling, applied using four different brominated reaction partners. The rate of the reaction showed to be highly affected by the reaction partner employed and increased as the electron-withdrawing character of the substituent increased. Additionally, a competing reaction involving the substitution of the pinaneboryl group with a substituent of the phosphine ligand limited the reaction yield and, in some cases, hindered the purification of the product. Even though the conditions for the coupling reaction could not be fully optimized, pure samples of compounds En-69 and En-71 were isolated, and their photophysical properties were briefly examined. We could additionally show that the coupling product En-72, obtained via substitution of the pinaneboryl substituent with a pyridine fragment, could be protonated with a chiral acid which led to the formation of a couple of diastereomers detectable via \(^1\)H-NMR. We, therefore, forecasted that if the reaction is performed with only one of the two diastereomers, this feature could be of potential interest to investigate the racemization of the chiral emitter under different reaction conditions. The synthesis of compound En-59 gave us the possibility to test on this family of chromophores the method reported by Winter and co-workers, which allows the insertion of a platinum transition metal center in the molecular scaffold. The reaction proved to be successful, and the solid-state structure of the complex was obtained by means of x-ray diffraction analysis of suitable single crystals. Even though in the work of this thesis it could not be possible to isolate an enantiomerically pure emitter, the designed synthesis path was successfully completed and highlighted the potential for this strategy for the intended goal.

Thanks to the above-mentioned synthesis procedures, a total of 13 different donor-spiro-acceptor compounds could be isolated. In all the synthesized chromophores, the boron-based spiro center proved to be stable under atmospheric conditions and assured the orthogonal arrangement of the donor and acceptor fragments. However, the obtained crystal structures showed that the acceptor moiety displayed a certain degree of flexibility despite the rigid constraints imposed by the spiro geometry. In some of the obtained structures, the fragment was, in fact, bent along the B-S or B-N vector, and two different conformations could be observed.

The analysis of the photophysical properties for the obtained emitters was performed by means of absorption ad fluorescence spectroscopy as well as TCSPC. These measurements were essential to evaluate if the fluorescence of the chromophores also occurred via TADF and enabled us to correlate the observed photophysical properties with the structural features of the chromophores. The most important connection that we intended to highlight was the dependency of the emission wavelength from the kind of donor and acceptor moieties present in the molecular structure. For this specific purpose, the results of the above-mentioned measurements were also correlated to the measured cyclic voltammograms. Indeed, our analysis confirmed that increasing the strength of either of the two fragments led to a reduction of the energy difference between the frontier orbitals and, therefore, to a red-shift of the observed emission wavelength. This behavior highlighted the possibility of tuning the emission wavelength of the chromophore by properly choosing or modifying the two fragments. However, it must be mentioned that the exchange of one of the moieties may only marginally affect the emission wavelength but greatly affect other parameters, e.g., the excited state’s lifetime. This aspect was evidenced by the comparison between compounds 55 and 56 reported in chapter 3.4.2.3.

Compound 55 stood out during the analysis of the photophysical properties of the emitters due to its extremely long excited state lifetime and related long-lasting photoluminescence. The mechanism at the
base of the unique behavior for this emitter could not be clearly elucidated. We hypothesized, however, that TADF with a slow rISC or RTP might be at the base of this chromophore’s emission. Further investigation on the photophysical properties of compound 55 is of high interest since it would allow us to fully understand the factors that induce the extended lifetime of the excited state and potentially lead to the rational synthesis of more chromophores with long-lasting luminescence.

Of all the examined emitters, nine compounds displayed a delayed emission when the measurements were performed in degassed solution. When embedded in a polymeric thin film, two additional compounds, 50 and 53, showed a delayed component. For almost all the examined emitters, the inclusion in thin films also increased the observed photoluminescence quantum yield. In fact, when measured in solution, this parameter did not exceed the value of 5%. However, when the emitters were dispersed in the polymeric matrices, values that ranged between 3% and 35% were recorded. The positive influence of the more rigid environment on the photophysical properties of the emitters was connected to the relative flexibility of the donor fragment that, in the absence of external constraints, could possibly facilitate the non-radiative relaxation of the excited state. Instead, in the rigid polymeric matrices, the flexibility of the donor fragment is restrained, leading to the observed positive effects. In terms of photoluminescence quantum yield, the performances displayed by the synthesized emitters were inferior compared to performances of the related compounds developed by Wu, Chou, Chi, and co-workers. This result demonstrated that using a bidentate donor fragment and, therefore, introducing a spiro center in correspondence with the boron atom did not lead to the expected improvement of performances. While the flexibility of the donor moiety may be the primary reason behind the low luminescence quantum yield of the emitters, it cannot be excluded that other factors are also playing a role. To help pinpoint the cause of the limited photoluminescence quantum yield, it would be helpful to determine the energy of the orbitals involved in the delayed fluorescence emission and the rate of the different processes involving the excited state. In fact, inefficient conversion of \(^{1}\text{CT}\) to \(^{1}\text{CT}\) could also be caused by an energetic misalignment between these states and LE. Also, the rigid donor spiro acceptor arrangement may excessively limit the overlap with the frontier orbitals leading to an excessively low oscillator strength for the fluorescence emission, which would drastically limit the efficiency of this radiative process.

### 6.1.1. Further developments

The reported results show that several aspects of this compound class deserve to be further investigated by performing additional measurements or can be subjected to improvement by new modifications of the molecular structure.

One of the most relevant and logical modifications that could be applied to the molecular scaffold is using a suitable bidentate donor moiety that would enable the construction of a five-member spiro ring at the donor fragment. This structural change would be the most direct way to quantify the influence of the rigidity of the donor fragment on the photophysical properties of the chromophores. A first attempt to synthesize such emitters via the same protocols used in this thesis failed, indicating that the synthesis approach must be optimized to obtain these new compounds. As exemplified in Fig. 181 with some examples, the fragments that we envisaged could be used for this purpose are substituted biphenyls, bithiophenes, and phenylthiophenes. The advantage of introducing an asymmetrical donor unit, as phenylthiophenes is the direct formation of an emitter with a chiral center in correspondence of the boron atom.
atom. Emitters with this donor moiety could, therefore, be used to continue the development of chiral emitters while possibly displaying an improved quantum yield.

In this work, it has been shown that compound Di-65 could be successfully used as a reactant in Suzuki-Miyaura coupling reactions. However, we are confident that the transformations in which this compound can take part are not limited to this example. For instance, the pinaneboryl fragment could be substituted with a nitrile, a hydroxyl substituent, or with an amino functionality. The search for alternative reactions in which compound Di-65 can be used as the starting material is of interest since it can provide alternative derivatizations of the donor fragment. As for the exchange of the donor or acceptor fragment, such modifications can be useful for modifying the emission wavelength of the emitter and inducing changes in other photophysical properties of the chromophore.

The involuntary synthesis of compound 159 showed that, like the derivatization of the donor moiety, alteration of the acceptor fragment could be used to tune the photophysical properties of the emitter. Therefore it could be relevant to investigate the modification of this molecular portion and the property of the obtained emitters. Additional modifications of the acceptor fragment could be performed via the [2+2]-photocycloaddition of compound 55 by using differently substituted olefines. Alternatively, a halogenated phenyl pyridine derivative could be used as the base for the acceptor fragment. The halogenated position could be then functionalized once the chromophores are fully synthesized, in analogy to the synthesis path developed in chapter 3.2.

Ultimately, the synthesis of compound En-76-trans demonstrated that it is possible to connect a platinum-based transition metal center to the molecular scaffold, and it gave access to a new potential class of chromophores. The investigation of the photophysical properties of this compound is of particular interest since the presence of a transition metal center is expected to have a substantial effect on the emission of the chromophores and related parameters. The presence of a heavy atom should strongly influence the ISC and rISC between 1CT and 3CT and ease the emission from the triplet excited state via phosphorescence. However, it is also possible that the presence of the transition metal center could compromise the formation of a charge-transfer excited state and completely alter the original emission of the chromophore. In analogy with the work performed by the research group of Winter and co-workers, the obtained platinum complex could be even further modified by substituting the bromine atom at the platinum center with another halogen or a different residue.195-199

In conclusion, the work dedicated to this class of emitters yielded a first insight into their synthesis and photophysical properties. We could highlight the strengths and weaknesses of these chromophores and obtain different derivatives whose emission wavelength cover a wide range of the visible spectrum. Additional experimental work should be performed to better understand the relationship between the structure and photophysical properties of these compounds and improve their performances in terms of photoluminescence quantum yield. Nonetheless, the information gathered in this work and the various
possible routes for the modification of the molecular scaffold provide a solid base to introduce targeted meliorative changes.

6.2. **Emitters of the class Spiro-C**

The establishment of a synthesis procedure towards the class of compounds *spiro-C* posed more challenges and required a more significant experimental effort in contrast to what had been reported for the class of compounds *spiro-B*. During the reported investigations, two different synthesis strategies were tested in which the boron center was either introduced at the beginning or at the end of the synthesis sequence. Additionally, two different reactions for the introduction of the borylene bridge in the molecular scaffold were examined. Specifically, the silicon/tin-boron exchange reaction or the direct combination of a metalated species with a boron electrophile.

From the performed investigations, we could establish that the best procedure for the construction of the molecular scaffold consisted of introducing the borylene bridge at the end of the synthesis pathway by combining the Grignard reagent 120-MgCl and diisopropylamino borane. The reported synthesis method gave access to compound 37-OH, whose purification was obtained via crystallization of its highly insoluble ethanolamine derivative. The borinic acid was considered a more convenient target compared to the corresponding isopropyl ester due to its higher stability against hydrolysis. This property facilitated its purification without undermining the possibility of derivatization of the boron center. The procedure for substituting the hydroxyl group in compound 37-OH with an aryl substituent proceeded over three synthesis steps. Firstly, the borinic acid was converted to the potassium difluoroborate salt 37-F$_2$K, which could also be used as a practical and stable storing form before applying the final two stages. Compound 37-F$_2$K was then reacted with TMS-Cl leading to the in-situ generation of compound 37-F, and the obtained fluoroborate was finally converted to the arylated product via the reaction with a suitable metalated species. In this thesis, the derivatization procedure was applied using mesityllithium as the metallated aryl derivative delivering compound 37-Mes.

The developed synthesis pathway and derivatization procedure are not limited to the synthesis of 37-Mes but can be potentially adapted to the production of different derivatives by using different metallated aryl or alkyl reagents. This characteristic fulfilled one of the requirements expressed in the aim of this thesis of obtaining a flexible and practical synthesis method. The third substituent R at the boron center of 37-R could be, in fact, easily varied at the end of the synthesis sequence without the need to establish a new synthesis route.

The analysis of the crystal structure of compounds 37-OH and 37-Mes confirmed that the donor and acceptor moieties in this class of compounds are orthogonally arranged, with only minor deviations. The brief investigation of the photophysical properties of compound 37-Mes confirmed that the observed fluorescence originates from a charge-transfer excited state and that part of the emission occurs via TADF. Therefore, it could be concluded that in compound 32, replacing the carbonyl group with a borylene bridge did not alter the peculiar properties of the emitters that we wanted to preserve.
6.2.1. Further developments

An additional aim of this work was the synthesis of different derivatives of compound 37-R, differing for the substituents at the boron center. The obtained series of compounds would have allowed us to analyze the influence that various substituents have on the photophysical properties of the chromophores. Unfortunately, during the work for this thesis, it was not possible to obtain and characterize different derivatives other than 37-Mes. For this reason, the investigation of this aspect should be the first task tackled by future studies involving this molecular scaffold. Substituents that could be used for this purpose are, for instance, the 1,3,5-tris(trifloromethyl)phenyl, naphthyl, or anthracenyl residues. Installation of these fragments at the boron center should still provide an adequate steric shielding of the boron center while yielding acceptors moieties with different electronic properties compared to the one equipped with the mesityl substituent. In analogy to what had been reported for the class spiro-B, a change of the acceptor strength should then lead to a change in the HOMO energy and consequently to a shift of the observed emission wavelength. An additional substitution that could be tested is the one reported by Yamaguchi and co-workers. This transformation would not simply involve the displacement of the hydroxyl group of 37-OH but the incorporation of the boron in a planar and rigid structure. In analogy to the previously illustrated functionalization, the first step for the construction of the planar scaffold is the reaction between a suitable lithiated substrate and a diarylbromo borane. This step is then followed by a cyclization reaction that ensures the completion of the rigid moiety. This synthetic sequence adapted to the specific case of compound 37-OH is reported in Fig. 182.

![Fig. 182 Synthesis strategy reported by Yamaguchi and co-workers for the inclusion of a tricoordinated boron atom in a planar rigid scaffold, adapted to the molecular backbone of the class of compounds spiro-C.](image)

The derivatization sequence developed in this chapter provides an easy tool for the modification of the acceptor fragment, but the same cannot be stated for the donor moiety. The lack of dedicated functional groups does not allow the derivatization of this portion of the molecule with a comparably straightforward procedure. However, in analogy to what had been discussed for the class spiro-B, two different strategies can be employed to modify the donor fragment. The triphenylamine fragment could be modified after the main molecular scaffold is created with a similar strategy to the one employed for the derivatization of compound 56. However, the adaptation of this reaction path and the choice of suitable reaction conditions may be hampered by the presence of the boron atom in its tricoordinate state. As already discussed in chapter 4.1.3, in this configuration, the heteroatom is more susceptible to nucleophilic attacks and oxidation, limiting its compatibility with different reaction conditions. A crucial point that must be considered in the adaptation of the derivatization procedure used in chapter 3.2 to this molecular scaffold is the stage at which the derivatization is performed. Applying the derivatization procedure before the substitution of the hydroxyl group at the boron atom is complete may compromise
the tricoordinate boron center. On the other hand, the presence of a substituent at the boron atom may reduce the regioselectivity of the derivatization and involve the newly attached substituent.

A more radical way to modify the donor fragment in the molecular scaffold is the complete substitution of the triphenylamine fragment with another moiety. However, this kind of strategy would significantly impact the synthesis sequence used to build the molecular scaffold itself. In the developed reaction sequence, the installation of the triphenylamine moiety is strongly connected to the tetra-substitution of the central carbon atom via the acid-catalyzed cyclization reaction. In the context of this thesis, no attempts to substitute the donor fragment were performed. However, the reactivity present in the literature suggests that the application of the same synthesis sequence could be extended to other donor fragments.\[462-465\] For instance, it should be possible to install a diphenyl sulfide, or diphenyl ether moiety, as well as a tert-butyl-substituted triphenyl fragment as in compound 50. Another possibility could be represented by the introduction of a diphenylamine fragment. In this case, the third substituent at the nitrogen atom could be installed at a subsequent stage. However, depending on which stage this reaction will be performed, its compatibility with the other functional groups present in the structure must be taken into account.

In conclusion, with the synthesis of compound 37-Mes, we could highlight the potential of the molecular scaffold 37-R as the base for the development of efficient TADF emitters. Additionally, the developed synthesis procedure allows a straightforward modification of the substituent at the boron center with different substituents. The number of accessible derivatives could be potentially increased by the development of a procedure for the substitution or derivatization of the donor moiety. Targeted modification of the molecular backbone could deliver TADF emitters with specific photophysical properties by carefully tuning different structural elements of the molecular structure. The high number of variations at which the molecular scaffold can be subjected highlights the versatility of the molecular structure, thereby motivating further investigation involving this class of compounds.
7. Experimental section

7.1. Syntheses

Unless otherwise specified, the syntheses were conducted under inert atmosphere by means of standard Schlenk techniques or in an MBraun Labstar glovebox operating under nitrogen atmosphere with monitored amounts of water and oxygen. Commercially available chemicals were used as received unless otherwise indicated. Solvents were distilled from the appropriate drying agents: THF (sodium-benzophenone), toluene (sodium-benzophenone), n-hexane (sodium), and DCM (calcium hydride). All the indicated solvents were stored under inert conditions over 4 Å molecular sieves and their water contents were attested to be below 10 ppm by means of coulometric Karl Fischer titrations (SI Analytics TitroLine 7500 KF trace). ²BuLi was titrated prior use with menthol (isomeric mixture) and 2,2'-bipyridine as indicator, Me₂SnCl₂ was sublimed under reduced pressure and stored under nitrogen atmosphere. Anhydrous MgBr₂ in THF (0.2 M) was freshly prepared prior use: to a suspension of Mg turnings in the appropriate amount of THF, a stoichiometric amount of 1,2-dibromoethane was slowly added dropwise, keeping the temperature constant at r.t. by means of a water bath. The reaction was considered complete after gas evolution ceased. 2-phenylbenzo[g]quinoline, 2-(2-dibromoborylphenyl)pyridine (38-Br), (2,4-difluorophenyl)pyridine borane dibromide complex (42), 2-(2-dibromoborylphenyl)quinoline (43), 2,4-2,2,2′-dilithio-diphenyl sulfide · 2 TMEDA, N,N-bis(2-lithiophenyl)methylamine · TMEDA, compound 126, compound 133, and 9,9-dimethyl-9,10-dihydro-9-silaanthracene-10-one (140) were synthesized according to previously reported procedures. Flash column chromatography was performed using the automated system Interchim puriFlash XS 420+ with selfpacked silica gel columns. The Rf values are referring to TLC plates with the same stationary phase. NMR spectra were recorded in deuterated solvents on Bruker Avance III-400 or Bruker Avance III HD-400 spectrometers. Chemical shifts are reported as dimensionless δ values in ppm and ¹H NMR spectra are referenced relative to residual protio-solvent signals (CD₂Cl₂: 5.32 ppm; CDCl₃: 7.26 ppm). The remaining nuclei are referenced using the unified scale as defined by IUPAC with the following values for Ξ: ¹¹B (Ξ = 32.083974; BF₃·OEt₂), ¹³C (Ξ = 25.145020; Me₄Si), ¹⁹F (Ξ = 94.094011; CCl₃F), ¹¹⁹Sn (Ξ = 37.290632; Me₄Sn). Carbon atoms directly bonded to boron are not always observed in the ¹³C(¹H) NMR spectra due to quadrupolar relaxation leading to considerable signal broadening. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, n. o. = not observed. HRMS (ESI+) were obtained using a Thermo Scientific Velos Pro mass spectrometer. Elemental analyses were performed on an Elementar vario EL cube.
7.1.1. Synthesis of the precursors for spiro-B emitters and of compound 83

7.1.1.1. Synthesis of 5,10,10-trimethyl-5,10-dihydrophenazastannin (40-Sn)

![Structure of 40-Sn](image)

The synthesis was performed following a modified version of the procedure reported by Kupchik and Periacciante. \(N,N\)-Bis(2-lithiophenyl)methylamine·TMEDA (1.90 g, 6.10 mmol) was suspended in 60 mL toluene. \(\text{Me}_2\text{SnCl}_2\) (1.31 g, 5.96 mmol) was dissolved in 40 mL toluene and added dropwise to the aforementioned suspension at r.t. The mixture turned from orange to colorless at the end of the addition. The suspension was then heated to reflux for 3 h and stirred at r.t. overnight. The reaction mixture was poured on ice and the aqueous phase was extracted with toluene (3 × 50 mL). The combined organic phases were dried over \(\text{MgSO}_4\), filtered, and the solvent was evaporated. The product was obtained as a colorless powder (1.30 g, 3.94 mmol, 66% yield). No further purification steps were needed and \(^1\)H NMR spectroscopic data are in agreement with those previously reported (\(^{13}\)C and \(^{119}\)Sn NMR data were not given).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.47 (2H, dd, \(J = 7.1 \) Hz, \(J = 1.7 \) Hz), 7.32 (2H, ddd, \(J = 8.2 \) Hz, \(J = 7.2 \) Hz, \(J = 1.8 \) Hz), 7.19 (2H, d, \(J = 8.2 \) Hz), 7.03 (2H, td, \(J = 7.1 \) Hz, \(J = 1.0 \) Hz), 3.47 (3H, s), 0.50 (6H, s, \(J_{\text{H}^{1\text{H}}\text{Sn}} = 60.3, J_{\text{H}^{1\text{H}}\text{Sn}} = 57.6\)).

\(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): \(\delta \) 153.80, 135.73, 132.10, 129.17, 121.98, 117.16, 40.07, −10.48.

\(^{119}\)Sn NMR (149 MHz, CDCl\(_3\)): \(\delta \) −117.87.

7.1.1.2. Synthesis of 10,10-dimethylphenothiastannin (49)

![Structure of 49](image)

The synthesis was performed following a modified version of the procedure reported by Meinema and Noltes. 2,2'-Dilithio-diphenyl sulfide·2TMEDA (1.20 g, 2.8 mmol) was suspended in 100 mL toluene. \(\text{Me}_2\text{SnCl}_2\) (0.61 g, 2.8 mmol) was dissolved in 40 mL toluene and added dropwise to the suspension at r.t. The turbid mixture turned from orange to colorless at the end of the addition. The suspension was then heated to reflux for 2 h and stirred at r.t. overnight. The reaction mixture was poured on ice and the aqueous phase was extracted with toluene (3 × 50 mL). The combined organic phases were dried over \(\text{MgSO}_4\), filtered, and the solvent was evaporated. Purification of the crude product via column
chromatography using "hexane as eluent ($R_f = 0.35$, "hexane) gave the desired product as a colorless solid (0.546 g, 1.64 mmol, 59% yield).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 7.70–7.63 (2H, m), 7.61–7.53 (2H, m), 7.30–7.22 (4H, m), 0.57 (6H, s, $J_{H^1}^Sn = 60.2$ Hz, $J_{H^17}Sn = 57.6$ Hz).

$^{13}$C{[H]} NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ 145.35, 143.26, 136.00, 130.42, 128.82, 126.98, −10.70.

$^{119}$Sn NMR (149 MHz, CD$_2$Cl$_2$): $\delta$ −105.32.

Anal. calc. for C$_{14}$H$_{14}$SSn (333.04 g/mol): C, 50.49; H, 4.24. Found: C, 50.48; H, 4.24.

7.1.1.3. Synthesis of tris(4-tert-butylphenyl)amine

![image]

The synthesis was performed following a modified version of the procedure reported by Rathore et al. A mixture of triphenylamine (14.7 g, 60 mmol), tert-butanol (46.7 g, 630 mmol), and trifluoroacetic acid (180 mL) was stirred at 50 °C overnight. During this time a green precipitate formed. A saturated aqueous NaHCO$_3$ solution was precooled in an ice-water bath and the reaction mixture was slowly added into this solution. The aqueous phase was extracted with toluene (3 × 100 mL) and the combined organic phases were dried over MgSO$_4$, filtered, and the solvent was removed under reduced pressure. The so obtained yellow solid was washed three times with "hexane. The desired compound was isolated as an off-white powder (21.0 g, 50.8 mmol, 85% yield). NMR spectroscopic data well match those previously reported.

7.1.1.4. Synthesis of 58

![image]

The synthesis was performed following a modified version of the procedure reported by Clark et al. Tris-(4-tert-butylphenyl)amine (5.0 g, 12 mmol) was dissolved in DCM (210 mL). N-Bromosuccinimide (4.5 g, 25.3 mmol) in DMF (48 mL) was added slowly and the solution was stirred at r.t. overnight. The solution was washed with water (5 × 100 mL) and the combined organic phases were dried over MgSO$_4$, filtered, and the solvent was evaporated. The product was obtained as an off-white powder (5.65 g, 9.89 mmol, 82% yield). NMR spectroscopic data well match those previously reported.
7.1.1.5. Synthesis of benzo[h]quinoline borane dibromide complex (44)

The synthesis was performed following a modified version of the procedure reported by Ishida et al.\(^{183}\) Benzo[h]quinoline (4.12 g, 23 mmol) and DIPEA (3.0 g, 23 mmol) were dissolved in CH\(_2\)Cl\(_2\) (100 mL) and the solution was cooled to 0°C by means of an ice bath. Under stirring, BBr\(_3\) (17.3 g, 69 mmol) was added dropwise, the reaction mixture becomes increasingly orange and precipitate starts to form after 2/3 of BBr\(_3\) were added. The ice bath was then removed and the reaction stirred at room temperature for 16 h. The solvent and the excess BBr\(_3\) are removed under vacuum, the crude solid is re-dissolved in CH\(_2\)Cl\(_2\) (250 mL) and saturated NaCO\(_3\) solution (100 mL) is cautiously added. The aqueous phase was extracted with CH\(_2\)Cl\(_2\) (3 × 50 mL), the combined organic phases were dried over MgSO\(_4\), filtered and the solvent evaporated. The crude product was recrystallized three times by adding n-hexane to CH\(_2\)Cl\(_2\) solutions obtaining the analytically pure product as a light-yellow solid (4.39 g, 12.6 mmol, 55% yield).

Anal. calc. for C\(_{13}\)H\(_8\)BBr\(_2\)N (348.832 g/mol): C, 44.76; H, 2.31; N, 4.02. Found: C, 44.72; H, 2.43; N, 4.17.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.13 (1H, d, J = 5.5 Hz), 8.59 (1H, d, J = 8.1 Hz), 8.08 (1H, d, J = 6.7 Hz), 8.04 (1H, d, J = 9.0 Hz) 7.96-7.84 (3H, m), 7.80 (1H, d, J = 9.0 Hz).

\(^{13}\)C\((^1\)H) NMR (151 MHz, CDCl\(_3\)): \(\delta\) 145.42, 141.90, 140.55, 132.95, 130.87, 130.14, 130.05, 128.71, 125.12, 125.02, 122.78, 122.11, n. o. (BC).

\(^{11}\)B NMR (128 MHz, CDCl\(_3\)): \(\delta\) -0.47.

7.1.1.6. Synthesis of 2-phenylbenzo[g]quinoline borane dibromide complex (45)

The synthesis was performed following the same procedure employed for compound 44, reacting 2-phenylbenzo[g]quinoline (0.256 g, 1.0 mmol), DIPEA (0.130 g, 1.0 mmol), and BBr\(_3\) (0.752 g, 3.0 mmol) in 15 mL DCM. The crude mixture was purified via crystallization, by adding n-hexane to a DCM solution of the crude material, obtaining the analytically pure product as an orange solid (0.378 g, 0.89 mmol, 89% yield).

Anal. calc. for C\(_{19}\)H\(_{12}\)BBr\(_2\)N (424.930 g/mol): C, 53.71; H, 2.85; N, 3.30. Found: C, 53.73; H, 2.89; N, 3.40.
1H NMR (400 MHz, CDCl₃): δ 9.76 (1H, s), 8.75 (1H, d, J = 8.8 Hz), 8.59 (1H, s), 8.31 (1H, d, J = 8.6 Hz), 8.06 (1H, d, J = 8.6 Hz), 8.02 (1H, d, J = 7.3 Hz), 7.96 (1H, d, J = 8.8 Hz), 7.91 (1H, d, J = 7.8 Hz), 7.44 (1H, t, J = 7.3 Hz), 7.69 (1H, t, J = 7.4 Hz), 7.63 (1H, t, J = 7.5 Hz), 7.47 (1H, t, J = 7.5 Hz).

13C{¹H} NMR (200 MHz, CDCl₃): δ 158.75, 145.83, 135.22, 135.07, 134.22, 133.71, 132.04, 130.39, 129.47, 128.93, 128.83, 128.54, 128.01, 127.82, 126.09, 123.14, 122.78, 114.26.

11B NMR (128 MHz, CDCl₃): δ -1.65.

7.1.1.7. Synthesis of 83

![Structure of 83](image)

The synthesis was performed following a modified version of the procedure reported by Ishida et al. Compound 44 (0.215 g, 0.62 mmol) was suspended in toluene (8 mL) and a 2 M solution of AlMe₃ (0.62 mL, 1.24 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 16 h and then quenched with water (20 mL). The aqueous phase was extracted with Ethyl acetate (3 × 10 mL), the combined organic phases were dried over MgSO₄, filtered and the solvent evaporated. The crude mixture was purified via column chromatography, using n-hexane and ethyl acetate as eluent and subsequently sublimed. The desired compound was obtained as a white solid in 75% yield (0.11 g, 0.5 mmol).

1H NMR (400 MHz, CD₂Cl₂): δ 8.73 (1H, dd, J = 5.3 Hz, J = 1.0 Hz), 8.40 (1H, dd, J = 8.0 Hz, J = 1.0 Hz), 8.0 (1H, d, J = 9.0 Hz), 7.88 (1H, dd, J = 6.2 Hz, J = 1.5 Hz), 7.81 (2H, m), 7.76 (1H, d, J = 9.0 Hz), 7.67 (1H, dd, J = 8.0 Hz, J = 5.3 Hz), 0.26 (6H, s).

13C{¹H} NMR (151 MHz, CD₂Cl₂): δ 163.6, 147.78, 140.94, 136.85, 132.95, 131.31, 130.90, 129.58, 126.98, 125.48, 122.58, 121.91, 121.65, 8.6.

11B NMR (128 MHz, CD₂Cl₂): δ 4.86.
7.1.2. Synthesis of spiro-B emitters

7.1.2.1. Synthesis of 36

![36](image)

The synthesis was performed following the same procedure employed for compound 1, reacting 5,10,10-trimethyl-5,10-dihydrophenazastannin (0.200 g, 0.61 mmol), 4 (0.197 g, 0.61 mmol), and AlCl₃ (0.008 g, 0.06 mmol) in 15 mL of DCM. The crude mixture was purified via column chromatography, using hexane and DCM as eluent that gave the pure product as a yellow solid (0.107 g, 0.31 mmol, 51% yield). (Rₓ = 0.4, DCM/hexane, 1:1).

HRMS (ESI, m/z) calc. for [C₂₄H₁₉BN₂+H]⁺: 347.1714, found: 347.1704.

Anal. calc. for C₂₄H₁₉BN₂ (346.24 g/mol): C, 83.26; H, 5.53; N, 8.09. Found: C, 83.02; H, 5.58; N, 8.10.

¹H NMR (400 MHz, CD₂Cl₂): δ 8.15 (1H, dt, J = 5.7 Hz, J = 1.0 Hz), 8.03–7.91 (3H, m), 7.53 (1H, d, J = 7.1 Hz), 7.47 (1H, td, J = 7.1 Hz, J = 1.2 Hz), 7.43 (1H, td, J = 7.3 Hz, J = 1.5 Hz), 7.24–7.15 (3H, m), 7.11 (2H, d, J = 8.2 Hz), 6.69–6.60 (4H, m), 3.64 (3H, s).

¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 156.69, 147.55, 143.99, 140.41, 137.26, 132.09, 131.16, 130.92, 127.10, 126.21, 122.56, 121.56, 119.20, 117.79, 112.60, 34.88, n. o. (BC).

¹¹B NMR (128 MHz, CD₂Cl₂): δ 0.02.

7.1.2.2. Syntheses of 51

![51](image)

5 (0.443 g, 1.33 mmol) and 4 (0.432 g, 1.33 mmol) were dissolved in 30 mL of DCM and, under stirring, AlCl₃ (0.017 g, 0.13 mmol) was added. The mixture was stirred overnight at r.t. and the solvent was evaporated. The crude product was recrystallized three times by adding hexane to DCM solutions to give a white solid (0.334 g, 0.96 mmol, 72% yield). (Rₓ = 0.17, DCM/hexane, 1:3).

HRMS (ESI, m/z) calc. for [C₂₃H₁₆BNS⁺]: 349.1091, found: 349.1090.

Anal. calc. for C₂₃H₁₆BNS (349.26 g/mol): C, 79.10; H, 4.62; N, 4.01. Found: C, 78.91; H, 4.59; N, 4.17.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.63 (1H, d, $J = 5.8$ Hz), 8.00–7.95 (2H, m), 7.93 (1H, d, $J = 7.5$ Hz), 7.71 (1H, d, $J = 7.2$ Hz), 7.48 (2H, d, $J = 7.5$ Hz), 7.46 (1H, m), 7.42 (1H, td, $J = 7.4$ Hz, $J = 0.9$ Hz), 7.21 (1H, td, $J = 6.1$ Hz, $J = 2.4$ Hz), 7.13 (2H, td, $J = 7.5$ Hz, $J = 1.3$ Hz), 6.90 (2H, t, $J = 7.4$ Hz), 6.69 (2H, d, $J = 7.4$ Hz).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 157.43, 144.65, 140.61, 138.17, 136.99, 132.90, 131.55, 131.41, 126.58, 126.51, 125.59, 124.95, 122.54, 121.56, 117.78, n. o. (BC).

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ 0.60.

### 7.1.2.3. Synthesis of 52

The synthesis was performed following the same procedure employed for compound 1, reacting 5,10,10-trimethyl-5,10-dihydrophenazastannin (0.100 g, 0.30 mmol), 42 (0.110 g, 0.30 mmol), and AlCl$_3$ (0.004 g, 0.03 mmol) in 10 mL of DCM. The crude mixture was purified via column chromatography (hexane/DCM gradient), which gave the analytically pure product as a yellow solid (0.034 g, 0.090 mmol, 30% yield). ($R_f = 0.19$, DCM/hexane, 1:3).

HRMS (ESI, m/z) calc. for [C$_{24}$H$_{17}$BF$_2$N$_2$+H]$^+$: 383.1526, found: 383.1515.

Anal. calc. for C$_{24}$H$_{17}$BF$_2$N$_2$ (382.22 g/mol): C, 75.42; H, 4.48; N, 7.33. Found: C, 75.39; H, 4.36; N, 7.56.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 8.19–8.13 (2H, m), 8.00 (1H, td, $J = 7.8$ Hz, $J = 1.5$ Hz ), 7.25–7.19 (3H, m), 7.12 (2H, d, $J = 8.2$ Hz), 7.01 (1H, dd, $J = 7.7$ Hz, $J = 2.2$ Hz), 6.86 (1H, ddd, $J = 10.8$ Hz, $J = 9.2$ Hz, $J = 2.2$ Hz), 6.69 (2H, td, $J = 7.1$ Hz, $J = 1.0$ Hz), 6.64 (2H, dd, $J = 7.3$ Hz, $J = 1.9$ Hz), 3.6 (3H, s).

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ 165.26 (dd, $J_{CF} = 255.7$ Hz, $J_{CF} = 8.7$ Hz), 160.01 (dd, $J_{CF} = 259.4$ Hz, $J_{CF} = 11.9$ Hz), 152.73 (d, $J_{CF} = 5.3$ Hz), 147.29, 144.17, 141.02, 131.95, 127.41, 122.60, 121.39 (d, $J_{CF} = 9.8$ Hz), 120.40 (dd, $J_{CF} = 7.6$ Hz, $J_{CF} = 2.3$ Hz), 119.34, 113.12 (dd, $J_{CF} = 19.3$ Hz, $J_{CF} = 3.3$ Hz), 112.79, 101.73 (dd, $J_{CF} = 27.6$ Hz, $J_{CF} = 23.8$ Hz), 34.90, n. o. (BC).

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ −106.19 (d, $J_{FF} = 9.5$ Hz), −114.10 (d, $J_{FF} = 9.5$ Hz).

$^{11}$B NMR (128 MHz, CD$_2$Cl$_2$): $\delta$ 0.14.
A solution of **58** (0.50 g, 0.88 mmol) in THF (30 mL) was cooled to −78 °C using an isopropanol-dry ice bath and °BuLi (2.4 M in °hexane, 0.73 mL, 1.8 mmol) was then added dropwise. The mixture was stirred at the same temperature for 1 h. After this time, MgBr₂ (0.20 M in THF, 7.3 mL, 1.5 mmol) was added dropwise, at the end of the addition the flask was removed from the cooling bath and stirred for 30 min at r.t. The reaction mixture was then slowly added to a solution of **38-Br** (0.237 g, 0.73 mmol) in THF (20 mL) via a PTFE cannula. After the addition, the mixture was stirred for 2 d at r.t. The reaction was then quenched with distilled water and the aqueous phase was extracted with toluene (3 × 50 mL). The combined organic phases were dried over MgSO₄, filtered, and the solvent was evaporated. The crude product was purified via column chromatography (°hexane/DCM gradient) to give an orange solid (0.137 g, 0.238 mmol, 33% yield). (Rf = 0.16, DCM/hexane, 1:3).

HRMS (ESI, m/z) calc. for [C₄₁H₄₅BN₂+H]^+: 577.3749, found: 577.3732.

Anal. calc. for C₄₁H₄₅BN₂ (576.64 g/mol): C, 85.40; H, 7.87; N, 4.86. Found: C, 85.37; H, 7.40; N, 4.90.

1H NMR (400 MHz, CDCl₃): δ 8.27 (1H, d, J = 5.7 Hz), 7.98 (2H, d, J = 7.8 Hz), 7.90 (1H, td, J = 7.7 Hz, J = 1.3 Hz), 7.70 (1H, d, J = 7.2 Hz), 7.64 (2H, d, J = 8.4 Hz), 7.49 (1H, td, J = 7.1 Hz, J = 1.0 Hz), 7.43 (1H, td, J = 7.4 Hz, J = 1.1 Hz), 7.36 (2H, d, J = 8.4 Hz), 7.14 (1H, ddd, J = 7.3 Hz, J = 5.6 Hz, J = 1.0 Hz), 6.99 (2H, dd, J = 8.7 Hz, J = 2.5 Hz), 6.69 (2H, d, J = 2.5 Hz), 6.32 (2H, d, J = 8.7 Hz), 1.46 (9H, s), 1.03 (18H, s).

13C {¹H} NMR (101 MHz, CDCl₃): δ 156.42, 150.30, 145.26, 144.87, 140.92, 140.66, 139.72, 137.16, 131.92, 131.03, 130.88, 129.95, 127.44, 125.95, 123.55, 122.28, 121.03, 117.23, 113.66, 34.76, 33.68, 31.56, 31.41, n. o. (BC).

11B NMR (128 MHz, CDCl₃): δ 0.58.
7.1.2.5. **Synthesis of 53**

The synthesis was performed following a modified version of the procedure employed for compound **36**. **44** (290 g, 0.83 mmol) and **40-Sn** (0.300 g, 0.91 mmol) were suspended in 13 mL of 1,2-dichlorobenzene and, under stirring, AlCl₃ (0.026 g, 0.20 mmol) was added. The mixture was stirred overnight at 65°C and the solvent evaporated. The residue was re-dissolved in CH₂Cl₂ (50 mL) and saturated NaCO₃ solution (50mL) is added, the aqueous phase was extracted with CH₂Cl₂ (3 × 25 mL), the combined organic phases were dried over MgSO₄, filtered and the solvent evaporated. The crude mixture was purified via flash column chromatography (n-hexane/DCM/triethylamine) and subsequently sublimed in a Kugelrohr apparatus. The analytically pure product was obtained as an orange solid (0.205 g, 0.55 mmol, 67% yield). (Rf = 0.53, DCM/hexane/triethylamine, 1:1:0,1).

**Anal. calc. for C₂₆H₁₉BN₂ (370.262 g/mol):** C, 84.34; H, 5.17; N, 7.57. **Found:** C, 84.32; H, 5.28; N, 7.65.

**¹H NMR (400 MHz, CD₂Cl₂):** δ 8.43 (1H, dd, J = 5.3 Hz, J = 1.1 Hz), 8.38 (1H, dd, J = 8.0 Hz, J = 1.1 Hz), 8.10 (1H, d, J = 9.0 Hz), 7.97-7.90 (2H, m), 7.88 (1H, dd, J = 6.4 Hz, J = 1.6 Hz), 7.82 (1H, d, J = 9 Hz), 7.47 (1H, dd, J = 8.0 Hz, J = 5.3 Hz), 7.19-7.25 (2H, m), 7.17 (2H, dd, J = 8.2 Hz, J = 0.9 Hz), 6.69 (2H, dd, J = 7.2 Hz, J = 1.8 Hz), 6.63 (2H, td, J = 7.0 Hz, J = 1.2 Hz), 3.71 (3H, s).

**¹³C{¹H} NMR (100 MHz, CD₂Cl₂):** δ 147.65, 146.59, 142.00, 137.18, 134.80, 132.45, 131.07, 131.03, 129.35, 129.26, 127.29, 125.07, 122.67, 122.51, 122.04, 119.26, 112.66, 34.89, n. o. (BC).

**¹¹B NMR (128 MHz, CD₂Cl₂):** δ 2.96.

7.1.2.6. **Synthesis of 54**

The synthesis was performed following the same procedure employed for compound **53**, reacting **43** (0.289 g, 0.77 mmol), **40-Sn** (0.383 g, 1.16 mmol), and AlCl₃ (0.027 g, 0.20 mmol) in 13 mL of 1,2-dichlorobenzene. The crude mixture was purified via flash column chromatography, using n-hexane, DCM and triethylamine as eluent. The material was subsequently crystalized from a DCM-hexane solution.
cooled at -25°C. The analytically pure product was obtained as red crystals (0.171 g, 0.43 mmol, 56% yield). 

\[(R_f = 0.63, \text{DCM/hexane/triethylamine, 1:2:0.15}).\]

**Anal. calc. for C\textsubscript{28}H\textsubscript{21}BN\textsubscript{2} (396.3 g/mol):** C, 84.86; H, 5.34; N, 7.07. Found: C, 84.68; H, 5.23; N, 7.08.

**1H NMR (400 MHz, CDCl\textsubscript{3}):** δ 8.51 (1H, d, \(J = 8.7\) Hz), 8.22 (1H, d, \(J = 8.7\) Hz), 8.03 (1H, m), 7.93 (1H, d, \(J = 8.3\) Hz), 7.88 (1H, dd, \(J = 9.4\) Hz, \(J = 1.8\) Hz), 7.47 (1H, m), 7.42 (2H, m), 7.34 (2H, m), 7.17 (2H, m), 7.11 (2H, d, \(J = 7.7\) Hz), 6.54 (2H, td, \(J = 7.1\) Hz, \(J = 1.0\) Hz), 6.36 (2H, dd, \(J = 7.2\) Hz, \(J = 1.4\) Hz), 3.76 (3H, s).

**13C\{1H\} NMR (101 MHz, CDCl\textsubscript{3}):** δ 159.99, 146.97, 141.80, 141.56, 135.12, 131.93, 131.83, 131.67, 130.61, 128.58, 127.91, 126.71, 126.63, 125.86, 124.00, 122.05, 119.14, 115.33, 112.60, 35.42, n. o. (BC).

**11B NMR (128 MHz, CDCl\textsubscript{3}):** δ 0.42.

**7.1.2.7. Synthesis of 55**

The synthesis was performed following the same procedure employed for compound 53, reacting 44 (1.443 g, 4.16 mmol), 49 (1.525 g, 4.58 mmol), and AlCl\textsubscript{3} (0.111 g, 0.83 mmol) in 45 mL 1,2-dichlorobenzene. The crude mixture was filter over a pad of silica using a hexane/DCM, 1:1 mixture as eluent and the obtained material was recrystallized three times by adding hexane to a DCM solution. The analytically pure product was obtained as a light-yellow solid (0.034 g, 0.090 mmol, 52% yield).

**Anal. calc. for C\textsubscript{25}H\textsubscript{16}BNS (373.280 g/mol):** C, 80.44; H, 4.32; N, 3.75; S, 8.59. Found: C, 80.38; H, 4.36; N, 3.85; S, 8.54.

**1H NMR (600 MHz, CD\textsubscript{2}Cl\textsubscript{2}):** δ 8.97 (1H, d, \(J = 5.4\) Hz), 8.49 (1H, d, \(J = 7.9\) Hz), 8.10 (1H, d, \(J = 9.0\) Hz), 7.95 (1H, d, \(J = 9.5\) Hz), 7.94 (1H, d, \(J = 10.4\) Hz), 7.87 (2H, m), 7.60 (1H, dd, \(J = 7.9\) Hz, \(J = 5.4\) Hz), 7.52 (2H, d, \(J = 7.8\) Hz), 7.13 (2H, td, \(J = 7.9\) Hz, \(J = 1.3\) Hz), 6.85 (2H, t, \(J = 7.3\) Hz), 6.66 (2H, d, \(J = 7.4\) Hz).

**13C\{1H\} NMR (151 MHz, CD\textsubscript{2}Cl\textsubscript{2}):** δ 147.54, 142.65, 138.16, 137.92, 134.14, 132.65, 131.31, 131.19, 129.46, 129.12, 126.56, 125.65, 125.33, 124.98, 122.90, 122.56, 122.17, n. o. (BC).

**11B NMR (128 MHz, CD\textsubscript{2}Cl\textsubscript{2}):** δ 3.57.
7.1.2.8. **Synthesis of 56**

The synthesis was performed following the same procedure employed for compound 53 reacting 43 (0.263 g, 0.70 mmol), 49 (0.351 g, 1.05 mmol), and AlCl₃ (0.018 g, 0.14 mmol) in 6 mL of 1,2-dichlorobenzene. The crude mixture was purified via flash column chromatography, using hexane, DCM and triethylamine as eluent. The analytically pure product was obtained as a yellow solid (0.219 g, 0.55 mmol, 78% yield). ($R_f = 0.54, \text{DCM/hexane/triethylamine, 1:2:0.15}$).

Anal. calc. for C₂₇H₁₈BNS (399.32 g/mol): C, 81.21; H, 4.54; N, 3.51; S, 8.03. Found: C, 80.94; H, 4.35; N, 3.58; S, 8.16.

$^1$H NMR (600 MHz, CDCl₃): δ 8.62 (1H, d, $J = 8.7$ Hz), 8.26 (1H, d, $J = 8.7$ Hz), 8.02 (1H, m), 7.97 (1H, dd, $J = 8.0$ Hz, $J = 1.3$ Hz), 7.86 (1H, m), 7.77 (1H, d, $J = 8.7$ Hz), 7.51 (1H, t, $J = 7.5$), 7.47 (2H, d, $J = 7.8$ Hz), 7.45 (1H, m), 7.31 (2H, m), 7.05 (2H, m), 6.71 (2H, td, $J = 7.4$ Hz, $J = 1.2$ Hz), 6.21 (2H, dd, $J = 7.5$ Hz, $J = 1.3$ Hz).

$^{13}$C$\{^1$H$\}$ NMR (150 MHz, CDCl₃): δ 160.94, 142.40, 141.10, 136.40, 134.60, 132.21, 132.11, 131.00, 130.22, 128.72, 127.92, 126.98, 126.23, 125.96, 125.27, 124.84, 124.59, 122.48, 115.44, n. o. (BC).

$^{11}$B NMR (128 MHz, CDCl₃): δ 0.58.

7.1.2.9. **Synthesis of 57**

The synthesis was performed following the same procedure employed for compound 53, reacting 45 (0.140 g, 0.42 mmol), 40-Sn (0.160 g, 0.38 mmol), and AlCl₃ (0.015 g, 0.11 mmol) in 5 mL 1,2-dichlorobenzene. The crude mixture was purified via crystallization by adding hexane to a DCM solution and the obtained material is subsequently sublimed in a Kugelrohr apparatus. The analytically pure product is obtained as an orange solid (0.127 g, 0.28 mmol, 73% yield).

Anal. calc. for C₃₁H₂₀BNS (449.378 g/mol): C, 82.86; H, 4.49; N, 3.12; S, 7.13. Found: C, 83.09; H, 4.54; N, 3.09; S 7.09.
$^1$H NMR (800 MHz, CDCl$_3$): $\delta$ 8.74 (1H, d, $J = 8.8$ Hz), 8.52 (1H, s), 8.37 (1H, s), 8.23 (1H, d, $J = 8.9$ Hz), 8.08 (1H, m), 7.96 (1H, d, $J = 8.3$ Hz), 7.84 (1H, m), 7.76 (1H, d, $J = 8.5$ Hz), 7.48 (3H, m), 7.44 (1H, m), 7.37 (2H, m), 7.03 (2H, m), 6.67 (2H, t, $J = 7.3$ Hz), 6.31 (2H, dd, $J = 7.6$ Hz, $J = 1.3$ Hz).

$^{13}$C($^1$H) NMR (201 MHz, CDCl$_3$): $\delta$ 168.83 (br), 161.55, 142.83, 142.43 (br), 136.92, 136.49, 135.45, 134.76, 132.54, 131.85, 131.47, 130.45, 129.14, 128.38, 127.79, 127.69, 126.96, 126.26, 126.04, 125.86, 125.13, 124.69, 122.84, 122.81, 114.90.

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ 0.68.
7.1.3. Derivatization of compound 56

7.1.3.1. Synthesis of En-59

Compound 56 (0.371 g, 0.93 mmol) was dissolved in DCM (30 mL) under normal atmospheric conditions. The reaction mixture was cooled with an ice bath and a solution of NBS (0.185 g, 1.04 mmol) was added over the course of 10 min with a syringe. The reaction flask was capped, the ice bath removed, and the reaction stirred for 15 h at r.t. The reaction was then quenched with distilled water and the aqueous phase was extracted with DCM (3 × 30 mL). The combined organic phases were dried over MgSO$_4$, filtered, and the solvent was evaporated. The crude product was purified via column chromatography (hexane/DCM gradient) to give a yellow solid (0.261 g, 0.55 mmol, 59% yield). ($R_f = 0.21$, DCM/hexane, 1:3). From the same purification procedure also compound 56 (0.021 g, 0.053 mmol) and 60 (0.062 g, 0.11 mmol, 12% yield) ($R_f = 0.29$, DCM/hexane, 1:3) were isolated.

Compound En-59:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.65 (1H, d, $J = 8.7$ Hz), 8.27 (1H, d, $J = 8.7$ Hz), 8.03-8.01 (1H, m), 8.00 (1H, dd, $J = 8.1$ Hz, $J = 1.5$ Hz), 7.80 (1H, m), 7.70 (1H, dd, $J = 8.7$ Hz, $J = 0.7$ Hz), 7.54 (1H, ddd, $J = 8.0$ Hz, $J = 6.9$ Hz, $J = 1.3$ Hz), 7.50 (1H, ddd, $J = 8.6$ Hz, $J = 7.0$ Hz, $J = 1.7$ Hz), 7.43 (1H, d, $J = 7.8$ Hz), 7.35-7.32 (2H, m), 7.32 (1H, d, $J = 8.5$ Hz), 7.15 (1H, dd, $J = 8.3$ Hz, $J = 2.3$ Hz), 7.04 (1H, ddd, $J = 7.9$ Hz, $J = 7.2$ Hz, $J = 1.5$ Hz), 6.70 (1H, td, $J = 7.3$ Hz, $J = 1.2$ Hz), 6.30 (1H, d, $J = 2.2$ Hz) 6.15 (1H, dd, $J = 7.6$ Hz, $J = 1.2$ Hz).

$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 161.18, 142.92, 141.88, 141.09, 136.06, 135.84, 134.76, 133.56, 132.53, 131.23, 130.30, 129.09, 129.04, 128.17, 127.33, 127.08, 126.66, 126.30, 125.38, 125.23, 124.47, 122.79, 119.33, 115.67, n. o. (BC).

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ 0.01.

Compound 60:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.68 (1H, d, $J = 8.7$ Hz), 8.28 (1H, d, $J = 8.7$ Hz), 8.06-8.00 (2H, m), 7.86-7.42 (1H, m), 7.65 (1H, dd, $J = 8.6$ Hz, $J = 0.8$ Hz), 7.57 (1H, ddd, $J = 7.8$ Hz, $J = 6.9$ Hz, $J = 1.3$ Hz), 7.53 (1H, ddd, $J = 8.5$ Hz, $J = 6.9$ Hz, $J = 1.6$ Hz), 7.36 (2H, m), 7.30 (2H, d, $J = 8.4$ Hz), 7.15 (2H, dd, $J = 8.4$ Hz, $J = 2.3$ Hz), 6.25 (2H, d, $J = 2.3$ Hz).

$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 161.23, 143.30, 140.88, 135.24, 134.76, 133.65, 132.79, 132.66, 130.22, 129.32, 129.25, 128.23, 127.51, 127.02, 126.94, 124.14, 122.96, 119.57, 115.76.
7.1.3.2. Synthesis of **Di-65**

![Diagram of Di-65]

Compound **En-59** (0.05 g, 0.11 mmol), diisopropylaminoborane (0.017 g, 0.15 mmol), triethylamine (0.021 g, 0.21 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.011 g, 0.016 mmol) were dissolved in dioxane (3 mL). The reaction mixture was stirred for 16 h at 80 °C and then the reaction solvent was evaporated under vacuum. A solution of (1S,2S,3R,5S)-(+)-pinanediol (0.070 g, 0.41 mmol) in MeOH (3 mL) was slowly added and the reaction mixture stirred for 30 min. The reaction mixture was dried, and the crude product purified via column chromatography (hexane/DCM gradient) to give a yellow-orange solid (0.028 g, 0.048 mmol, 46% yield) ($R_f = 0.37$, DCM/petroleum ether, 1:1).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.64 (1H, dd, $J_{11} = 11.0$ Hz, $J_{9,0} = 9.0$ Hz), 8.29 (1H, dd, $J_{8,8,Hz} = 8.8$ Hz, $J_{6,3} = 6.3$ Hz), 8.09 (1H, d, $J_{7,3} = 7.3$ Hz), 8.00 (1H, dd, $J_{12,1} = 12.1$ Hz, $J_{8,0} = 8.0$ Hz), 7.76 (1H, dd, $J_{13,5} = 13.5$ Hz, $J_{8,7} = 8.7$ Hz), 7.70 (1H, dd, $J_{30,4} = 30.4$ Hz, $J_{6,5} = 6.5$ Hz), 7.56-7.44 (4H, m), 7.41 (1H, $t$, $J_{7,6} = 7.6$ Hz), 7.39-7.32 (2H, m), 7.04 (1H, dddd, $J_{7,9} = 7.9$ Hz, $J_{7,1} = 7.1$ Hz, $J_{6,0} = 6.0$ Hz), 6.72 (1H, s), 6.69 (1H, $t$, $J_{7,4} = 7.4$ Hz), 6.10 (1H, dddd, $J_{20,5} = 20.5$ Hz, $J_{7,5} = 7.5$ Hz, $J_{1,3} = 1.3$ Hz), 4.18 (1H, dddd, $J_{10,8} = 10.8$ Hz, $J_{8,8} = 8.8$ Hz, $J_{1,9} = 1.9$ Hz), 2.23 (1H, m), 2.03 (1H, m), 1.93 (1H, td, $J_{5,5} = 5.5$ Hz, $J_{1,7} = 1.7$ Hz), 1.78 (1H, m), 1.69 (1H, tdd, $J_{13,9} = 13.9$ Hz, $J_{3,2} = 3.2$ Hz, $J_{2,0} = 2.0$ Hz), 1.25 (3H, d, $J_{19,4} = 19.4$ Hz), 1.21 (3H, s), 0.95 (1H, d, $J_{10,9} = 10.9$ Hz), 0.77 (3H, s).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$): $\delta$ 163.59, 163.44, 145.48, 145.42, 143.56, 143.53, 143.23, 143.11, 140.32, 139.91, 138.81, 138.70, 137.67, 137.50, 135.26, 134.68, 134.67, 134.62, 134.59, 133.80, 133.48, 132.25, 132.16, 131.76, 131.75, 130.85, 130.84, 129.68, 129.65, 129.04, 129.01, 128.74, 128.71, 127.63, 127.55, 127.51, 127.44, 127.21, 127.11, 126.59, 126.45, 125.64, 125.56, 118.49, 118.47, 88.45, 88.38, 80.46, 80.42, 53.91, 53.89, 42.08, 42.07, 42.06, 41.62, 37.91, 37.87, 30.94, 30.90, 29.39, 29.38, 28.83, 28.76, 26.30, n. o. (BC).

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ 29.27, 0.40.

7.1.3.3. Synthesis of **En-69**

![Diagram of En-69]

**Di-65** (0.020 g, 0.038 mmol), 4-bromoanisole (0.008 g, 0.043 mmol), K$_2$CO$_3$ (0.01 g, 0.072 mmol), palladium(II) acetate (0.002 g, 0.009 mmol) and triphenylphosphine (4 g, 0.015 mmol) were added to a 1:2 methanol/acetonitrile mixture (6.5 mL) and the suspension was stirred for 16 h at 80 °C. The reaction was then quenched with distilled water and the aqueous phase was extracted with DCM (3 × 5 mL). The
combined organic phases were dried over MgSO₄, filtered, and the solvent was evaporated. The crude product was purified via column chromatography (hexane/DCM gradient) to give a yellow solid (0.005 g, 0.01 mmol, 25% yield).

\[ \text{H NMR (600 MHz, CD}_2\text{Cl}_2):} \delta 8.72 (1H, d, J = 8.7 Hz), 8.33 (1H, d, J = 8.7 Hz), 8.10 (1H, dd, J = 8.1 Hz, J = 1.4 Hz), 8.09 (1H, m), 7.81 (1H, m), 7.77 (1H, d, J = 8.8 Hz), 7.57 (1H, ddd, J = 8.1 Hz, J = 6.9 Hz, J = 1.1 Hz), 7.50 (1H, ddd, J = 8.7 Hz, J = 6.9 Hz, J = 1.5 Hz), 7.49 (1H, d, J = 8.1 Hz), 7.44 (1H, dd, J = 7.8 Hz, J = 0.7 Hz), 7.34 (2H, pd, J = 7.2 Hz, J = 1.5 Hz), 7.26 (1H, ddd, J = 8.1 Hz, J = 2.2 Hz), 7.05 (1H, ddd, J = 7.9 Hz, J = 7.1 Hz, J = 1.5 Hz), 6.97 (1H, m), 6.97 (1H, d, J = 8.9 Hz), 6.72-6.67 (2H, m), 6.68 (1H, d, J = 6.7 Hz), 6.37 (1H, d, J = 2.3 Hz), 6.18 (1H, dd, J = 7.5 Hz), 3.69 (3H, s).

\[ \text{C{[H]} NMR (151 MHz, CD}_2\text{Cl}_2):} \delta 163.72, 161.25, 145.52, 143.57, 139.75, 139.06, 137.80, 137.44, 136.30, 134.65, 134.54, 133.38, 132.14, 131.73, 131.55, 130.83, 130.07, 129.72, 129.00, 128.63, 128.15, 127.84, 127.47, 127.16, 126.80, 125.56, 118.44, 116.32, 57.75.

\[ \text{B NMR (128 MHz, CDCl}_3):} \delta 0.27.

7.1.3.4. Synthesis of En-71

The synthesis was performed following the same procedure employed for compound En-69, reacting Di-65 (0.037 g, 0.064 mmol), 4-bromobenzotrifluoride (0.020 mg, 0.09 mmol), K₂CO₃ (0.018 g, 0.128 mmol), palladium(II) acetate (0.003 g, 0.013 mmol) and tri(o-tolyl)-phosphine (0.008 g, 0.026 mmol) in 6.5 mL of a 1:2 methanol/acetonitrile mixture. The reaction mixture was stirred for 1 h at 50°C. The crude product was purified via column chromatography (hexane/DCM gradient) to give a yellow solid (0.011 g, 0.020 mmol, 31% yield).

\[ \text{H NMR (400 MHz, CD}_2\text{Cl}_2):} \delta 8.72 (1H, d, J = 8.8 Hz), 8.34 (1H, d, J = 8.7 Hz), 8.09 (1H, m), 8.06 (1H, dd, J = 8.3 Hz, J = 1.3 Hz), 7.81 (1H, m), 7.77 (1H, d, J = 8.7 Hz), 7.60-7.54 (1H, m), 7.56 (1H, d, J = 8.2 Hz), 7.50 (1H, ddd, J = 8.6 Hz, J = 7.0 Hz, J = 1.7 Hz), 7.46 (1H, dt, J = 7.8 Hz, J = 0.6 Hz), 7.41 (2H, dd, J = 8.1 Hz, J = 0.7 Hz), 7.35 (3H, m), 7.18 (2H, dd, J = 8.1 Hz, J = 0.7 Hz), 7.07 (1H, ddd, J = 7.8 Hz, J = 7.2 Hz, J = 1.5 Hz, J = 0.8 Hz), 6.73 (1H, tt, J = 7.4 Hz, J = 0.8 Hz), 6.44 (1H, d, J = 2.1 Hz), 6.21 (1H, dd, J = 7.5 Hz, J = 1.1 Hz).

\[ \text{C{[H]} NMR (101 MHz, CD}_2\text{Cl}_2):} \delta 161.59, 145.33, 143.43, 141.34, 137.80, 136.54, 136.38, 135.23, 132.51, 132.41, 131.24, 129.96, 129.93, 129.60, 128.65, 127.56, 127.21, 126.91, 126.55, 126.19, 125.67, 125.63, 125.59, 125.56, 125.47, 125.39, 124.52, 123.41, 116.25., n.o. (BC).

\[ \text{B NMR (128 MHz, CDCl}_3):} \delta 0.32.

\[ \text{F NMR (376 MHz, CDCl}_3):} \delta -62.45
7.1.3.5. Attempt of synthesizing En-72

The synthesis was performed following the same procedure employed for compound En-69, reacting Di-65 (0.072 g, 0.12 mmol), 4-bromopyridine (0.028 g, 0.18 mmol), K$_2$CO$_3$ (0.033 g, 0.24 mmol), palladium(II) acetate (0.005 g, 0.024 mmol), and tri(o-tolyl)-phosphine (0.014 g, 0.048 mmol) in 6 mL of a 1:2 methanol/acetonitrile mixture. The reaction mixture was stirred for 2 h at 55°C. The crude product was purified two times via column chromatography (DCM/methanol gradient) to give 0.046 g of a yellow solid which was, however, not analytically pure and contained small amounts of unknown impurities together with grease and dichloromethane which hindered an accurate estimation of the reaction yield.

$^1$H NMR (400 MHz, THF-d$_8$): δ 8.86 (1H, d, J = 8.7 Hz), 8.53 (1H, d, J = 8.7 Hz), 8.29 (1H, d, J = 4.5 Hz), 8.17 (1H, d, J = 7.5 Hz), 8.08 (1H, dd, J = 7.5 Hz, J = 1.8 Hz), 7.80 (2H, m), 7.73 (1H, d, J = 7.0 Hz), 7.50 (2H, m), 7.45 (1H, d, J = 8.2 Hz), 7.39 (1H, td, J = 7.9 Hz, J = 1.7 Hz), 7.35 (1H, d, J = 7.9 Hz), 7.26 (2H, m), 7.13 (1H, d, J = 8.0 Hz), 6.95 (2H, m), 6.91 (1H, ddd, J = 7.5 Hz, J = 4.8 Hz, J = 0.7 Hz), 6.60 (1H, td, J = 7.5 Hz, J = 1.0 Hz), 6.14 (1H, d, J = 7.5 Hz).

$^{11}$B NMR (128 MHz, THF-d$_8$): δ 0.05.

7.1.3.6. Attempt of synthesizing En-76-trans

The synthesis was performed following a modified version of the procedure reported by Winter and co-workers.$^{134}$ cis-Pt(Et)$_2$(P(Et)$_3$) (0.02 g, 0.04 mmol) was dissolved in C$_6$D$_6$ (1 mL) and the solution was heated at 110 °C for 1 h. The solution was then let cool to r.t. and compound En-59 (0.02 g, 0.04 mmol) was added as a solid and the solution mixed until its dissolution. The reaction mixture was heated at 50 °C for 1 h and then at 70 °C for 4 h. The solvent was then evaporated, and the crude mixture was purified via column chromatography, using "hexane and ethyl acetate as eluent ($R_f$ = 0.13 ethyl acetate/"hexane 1:3).

$^1$H NMR (400 MHz, C$_6$D$_6$): δ 8.15 (1H, d, J = 8.5 Hz), 7.95 (1H, dd, J = 5.8 Hz, J = 1.6 Hz), 7.69 (1H, d, J = 7.9 Hz), 7.67 (1H, dd, J = 6.0 Hz, J = 1.9 Hz), 7.60 (1H, d, J = 8.7 Hz), 7.47 (1H, d, J = 8.6 Hz), 7.39 (1H, d, J = 7.9 Hz), 7.21-7.05 (4H, m, partially superimposed with the solvent signal), 7.02 (1H, td, J = 7.6 Hz, J = 1.6
Hz), 6.82-6.68 (3H, m), 6.58 (1H, dd, $J = 7.5$ Hz, $J = 1.3$ Hz), 6.26 (1H, s, $J_{1}^{195}P_{Pt} = 60.6$ Hz), 1.45-1.04 (12H, m), 0.72 (9H, m), 0.55 (9H, m).

$^{31}B$ NMR (128 MHz, $C_6D_6$): $\delta$ 0.68.

$^{31}P$ NMR (128 MHz, $C_6D_6$): $\delta$ 12.44 (d, $J = 7.5$ Hz satellites with $J = 2803$ Hz)
7.1.4. Synthesis of the precursor for the preparation of 37-OH

7.1.4.1. Synthesis of 121

The synthesis was performed following a modified version of the procedure reported by Kawatsura and co-workers. A suspension of diphenylamine (2.0 g, 11.8 mmol), 2-bromiodobenzene (1.3 mL, 10.12 mmol), sodium tert-butoxide (2.36 g, 24.60 mmol), and copper iodide (0.488 g, 2.60 mmol) in THF (12 mL) was heated to 65°C for 17 h in a pressure vessel. The mixture was then quenched with a saturated potassium hydrogen carbonate solution and extracted with DCM (3 × 40 mL). The organic phase was filtered from the solid, dried with MgSO₄, and the solvent evaporated. The crude product was purified using column chromatography, which yielded a clear oil that slowly solidified (1.64 g, 5.06 mmol, 50% yield). Alternatively, the purification can also be performed via Kugelrohr distillation. This method yielded the pure product in 29% yield and other mixed fractions. The obtained material was characterized by means of NMR spectroscopy, and the obtained signals matched the one reported in the literature.

7.1.4.2. Synthesis of 127-Li·Et₂O

The synthesis was performed following a modified version of the procedure reported by Roesler Piers and Parvez. A solution of 121 (1.058 g, 3.26 mmol) in diethylether (30 mL) was cooled with an ice bath. A 3.2 M solution of n-BuLi in n-hexane (1 mL, 3.2 mmol) was added dropwise, and the mixture was stirred at room temperature for 16 h. After this time a white precipitate formed, the solvent was reduced to 20 mL, and the mixture filtered over a frit. The obtained solid was washed with n-hexane (10 mL) and then dried under vacuum. The product was obtained as a white powder (0.583 g, 1.79 mmol, 56% yield). The characterization of the compound was performed by means of 1H NMR spectroscopy, using standard THF as the solvent and two glass capillaries containing DMSO-d₆ as reference for the measurement. The NMR spectrum was referenced by setting the value of the THF peak at highest ppm to 3.63 ppm (corresponding to THF in THF-d8).

1H NMR (400 MHz, THF): δ 7.85 (1H, dd, J = 6.6 Hz, J = 1.5 Hz), 7.11 (4H, d, J = 8.0), 6.99 (4H, t, J = 7.8), 6.76 (1H, t, J = 7.3 Hz), 6.70 (1H, t, J = 6.6 Hz), 6.67–6.58 (3H, m), 3.40 (4H, q, J = 7.0 Hz), 1.13 (6H, t, J = 7.0 Hz).
7.1.4.3. **Synthesis of 123-Br**

![123-Br](image)

**Method 1**

The synthesis was performed following a modified version of the procedure reported by Chang et al., and all the synthesis steps were conducted under normal atmospheric conditions. To a solution of 126 (0.766 g, 2.24 mmol) in DCM (25 mL) were added PCC (1.45 g, 6.72 mmol) and Celite (1.1 g). The reaction mixture was stirred for 16 h at r.t. The reaction mixture was then filtered over a pad of celite, and the solvent evaporated. The crude mixture was purified via column chromatography, using an 8:1 hexane/Ethylacetate mixture as eluent. The pure product was obtained as a white solid in 57% yield (1.92 g, 5.65 mmol). The product was characterized by GC-MS and NMR spectroscopy, and the obtained signals matched the one reported in the literature.

**Method 2**

The synthesis was performed following a modified version of the procedure reported by Zhang and co-workers, and all the synthesis steps were conducted under normal atmospheric conditions. Benzophenone (0.4 g, 2.2 mmol), NBS (1.018 g, 5.72 mmol), palladium (II) acetate (0.128 g, 0.572 mmol) and potassium peroxodisulfate (1.78 g, 6.6 mmol) were suspended in dichloroethane (20 mL). Trifluoromethanesulfonic acid (0.51 mL, 5.72 mmol) was slowly added with a Pasteur pipette (plastic syringes are easily corroded) and the mixture heated for 18 h at 85°C. The suspension was then added to a saturated sodium hydrogen carbonate solution (50 mL) and the aqueous phase was adjusted to neutral pH by addition of a 1 M HCl solution. The two phases were separated, and the aqueous phase extracted with DCM (4 × 50 mL). The organic phase was filtered over celite and washed with water (4 × 100 mL). The solution was dried over MgSO₄, filtered and the solvent evaporated. The crude material was washed with a hexane/ethyl acetate mixture and then sublimed at 120°C under dynamic vacuum. The desired product was obtained as white solid in 56% (0.418 g, 1.23 mmol). The material was characterized by GC-MS and NMR spectroscopy, and the obtained signals matched the one reported in the literature.

7.1.4.4. **Synthesis of 123-Cl**

![123-Cl](image)

The synthesis was performed following the same procedure employed for compound 123-Br, reacting benzophenone (8.0 g, 43.89 mmol), N-chlorosuccinimide (14.0 g, 104.85 mmol), palladium (II) acetate (1.2 g, 5.35 mmol), potassium peroxodisulfate (27.0 g, 99.88 mmol), and trifluoromethanesulfonic acid (10.0 mL, 111.25 mmol) in dichloroethane (300 mL). The crude mixture was purified via distillation under reduced pressure, using a Vigreux column. Isolating the fraction that boils at 115°C at a pressure of 2·10⁻³ bar yielded the pure product as a yellow oil that crystallized overnight (7.41 g, 29.54 mmol, 67% yield). The product was characterized by GC-MS and NMR spectroscopy, and the obtained signals matched the one reported in the literature.
7.1.4.5. **Synthesis of 124-Cl**

A solution of 121 (1.787 g, 5.51 mmol) in THF (50 mL) was cooled to −78°C using an isopropanol-dry ice bath and n-BuLi (2.55 M in n-hexane, 4.39 mL, 11.02 mmol) was then added dropwise over 1 h. The cooling bath was removed, and the reaction mixture stirred at room temperature for 45 min. A solution of 123-Cl (1.26 g, 5.02 mmol) in THF (10 mL) was then added to reaction and the solution stirred for 16 h. 1/3 of the solvent of the obtained white suspension was evaporated under vacuum and the solid filtered over a frit. The obtained solid was washed with n-hexane (15 mL) and suspended in distilled water (50 mL). The pH of the aqueous phase was adjusted to 7 adding a saturated solution of ammonium chloride and DCM (100 mL) was added. The biphasic mixture was stirred until dissolution of the solid and then the two phases were separated. The aqueous phase was washed with DCM (2 × 50 mL), the organic phase was dried with MgSO₄ and the solvent evaporated. The obtained solid was washed with cold ethyl acetate (10 mL) and dried under vacuum. The product was obtained as a white solid (1.75 g, 3.53 mmol, 70% yield).

1H NMR (400 MHz, CDCl₃): δ 7.55 (1H, s), 7.37 (1H, td, J = 7.8 Hz, J = 1.6 Hz), 7.28 (3H, q, J = 8.5 Hz), 7.15 (2H, m), 7.06 (5H, m), 6.91 (9H, m), 6.71 (1H, t, J = 7.6 Hz), 6.53 (1H, d).

13C{1H} NMR (101 MHz, CDCl₃): δ 151.36, 149.12, 148.63, 143.91, 143.72, 142.91, 137.16, 136.86, 135.39, 134.63, 134.52, 134.41, 134.03, 133.43, 131.66, 131.50, 131.46, 131.44, 131.18, 128.52, 128.47, 128.27, 127.85, 126.73, 125.02, 124.43, 87.06.

7.1.4.6. **Synthesis of 119-Cl**

To a solution of 124-Cl (2.2 g, 4.43 mmol) in DCM (130 mL) was added BF₃ methyl etherate (2 mL, 21.76 mmol) and the solution stirred for 16 h at room temperature. Completion of the reaction was confirmed by TLC analysis (n-hexane-ethyl acetate 2-0.1, Rf = 0.5) and the solvent with the excess BF₃ methyl etherate was evaporated under vacuum. The crude material was dissolved in DCM (5 mL) and precipitated with ethanol (20 mL). The obtained solid was washed again with ethanol (2 × 20 mL) and dried under vacuum, the product was obtained as a white powder (1.86 g, 3.89 mmol, 88% yield).
\( ^{1}H \) NMR (400 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 7.54 (2H, m), 7.47 (1H, \( J = 7.4 \) Hz), 7.42 (2H, dd, \( J = 7.8 \) Hz, \( J = 1.4 \) Hz), 7.31 (2H, td, \( J = 7.6 \) Hz, \( J = 1.7 \) Hz), 7.20 (2H, m), 7.05 (4H, m), 6.98 (2H, dd, \( J = 7.9 \) Hz, \( J = 1.5 \) Hz), 6.85 (2H, m), 6.77 (2H, dd, \( J = 8.0 \) Hz, \( J = 1.6 \) Hz), 6.48 (2H, dd, \( J = 8.2 \) Hz, \( J = 1.0 \) Hz).

\( ^{13}C\{^{1}H\} \) NMR (151 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 144.88, 143.00, 141.79, 137.97, 135.65, 135.00, 133.74, 132.97, 132.95, 131.35, 130.86, 129.64, 128.89, 128.17, 122.23, 116.81, 60.81.

7.1.4.7. *Synthesis of 134-OH*

![Image of structure 134-OH]

Mg powder (1.9 g, 3.14 mmol) was suspended in 100 mL of THF and activated by adding dibromoethane 0.59 g, 3.14 mmol) and stirring the suspension for two minutes. A solution of diisopropylaminoborane (2.3 g, 20.4 mmol) and 133 (5.11 g, 15.7 mmol) in 15 mL THF was then added dropwise to the magnesium suspension. The reaction flask was closed, and the mixture heated at 65°C for 16 h. The reaction was quenched with ice and the water phase acidified using a 3 M solution of HCl. The aqueous phase was extracted three times with ethyl acetate (3 \( \times \) 50 mL), the combined organic phases were dried over MgSO\(_4\), filtered, and the solvent was evaporated. The crude product was purified via column chromatography (DCM/\(^{n}\)Hexane/methanol gradient) to give a white solid (1.76 g, 0.238 mmol, 58% yield). (Rf = 0.49, DCM/\(^{n}\)Hexane/MeOH, 1:3:0.2). Care must be taken to not overload the column since crystallization of the pure product in the eluent mixture easily occurs. This event can cause the clogging of the apparatus used for the separation especially if an automatized chromatographic system is used.

\( ^{1}H \) NMR (400 MHz, DMSO-\( d_6 \)): \( \delta \) 9.77 (1H, s), 8.10 (2H, dd, \( J = 7.4 \) Hz, \( J = 1.0 \) Hz), 7.49 (2H, td, \( J = 7.4 \) Hz, \( J = 1.5 \) Hz), 7.43 (2H, d, \( J = 7.2 \) Hz), 7.32 (2H, m), 4.31 (2H, s).

\( ^{13}C\{^{1}H\} \) NMR (151 MHz, DMSO-\( d_6 \)): \( \delta \) 147.82, 132.37, 131.30, 128.51, 125.61, 36.89, n. o. (BC).

\( ^{11}B \) NMR (128 MHz, DMSO-\( d_6 \)): \( \delta \) 39.77.

7.1.4.8. *Synthesis of 134-DMEA*

![Image of structure 134-DMEA]

To synthesize compound 134-DMEA, the crude reaction mixture obtained from the previous procedure was not purified and treated according to the procedure. The crude material (obtained from 0.328 g, 1 mmol of 133) was suspended in methanol (10 mL) and N,N-dimethylethanolamine (0.2 g, 2.24 mmol) were added. The solution is stirred at 40°C for 15 min and then the solvent evaporated. The crude material is washed several times with a \(^{n}\)hexane/ethyl acetate mixture and the pure product is obtained as a white solid in 57% yield (0.152 g, 0.57 mmol).

\( ^{1}H \) NMR (400 MHz, C\(_6\)D\(_6\)): \( \delta \) 7.90 (2H, t, \( J = 5.2 \) Hz), 7.32 (2H, m), 7.28 (4H, m), 4.07 (2H, m), 3.93 (2H, s), 2.16 (2H, t, \( J = 5.2 \) Hz), 1.42 (6H, s).
$^1$H NMR (101 MHz, C$_6$D$_6$): $\delta$ 146.12, 134.97, 129.82, 129.22, 127.78, 64.73, 61.57, 47.79, 43.06, n. o. (BC).

$^1$B NMR (128 MHz, DMSO-$d_6$): $\delta$ 7.51.

7.1.4.9. **Synthesis of 135-OH**

![Chemical Structure](image)

This procedure was performed under normal atmospheric conditions. To a solution of 134-OH (0.9 g, 4.64 mmol) in methanol (30 mL) was added DDQ (2.32 g, 10.21 mmol) as a solid, in small portions and the solution stirred at room temperature for 3.5 h. The solvent was evaporated, and the crude mixture suspended in chloroform (50 mL), the suspension is stirred with basic water (100 mL) for five minutes and then the aqueous phase was brought to acid pH adding a 3 M HCl solution. The organic phase was separated, and the water phase washed with chloroform (2 x 30 mL). The combined organic phases were dried over MgSO$_4$, filtered, and the solvent was evaporated. The crude product was purified via column chromatography (DCM/methanol/triethylamine gradient, Rf = 0.5, DCM/MeOH, 1: 0.1). After the separation, the collected fractions containing the product are washed with a 3 M HCl solution (3 x 50 mL) to remove the free and coordinated triethylamine. The organic phase was then dried over MgSO$_4$, filtered, and the solvent was evaporated. The product was obtained as an off-white powder (0.466 g, 2.24 mmol, 48% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.34 (1H, s), 8.18 (4H, m), 7.72 (4H, m).

$^1$C($^1$H) NMR (151 MHz, DMSO-$d_6$): $\delta$ 187.48, 139.65, 132.65, 131.95, 131.81, 127.08, n. o. (BC).

$^1$B NMR (128 MHz, DMSO-$d_6$): $\delta$ 35.77.

7.1.4.10. **Synthesis of 135-OB**

![Chemical Structure](image)

Compound 135-OH was heated at 130°C under vacuum until no evolution of water was observed via the vacuum gauge. The desired product was obtained with a quantitative yield.

$^1$H NMR (400 MHz, C$_6$D$_6$): $\delta$ 8.62 (2H, ddd, $J = 7.9$ Hz, $J = 1.1$ Hz, $J = 0.6$ Hz), 7.60 (2H, ddd, $J = 7.4$ Hz, $J = 1.3$ Hz, $J = 0.5$ Hz), 7.22 (2H, td, $J = 7.6$ Hz, $J = 1.4$ Hz), 7.04 (2H, td, $J = 7.4$ Hz, $J = 1.2$ Hz).

$^{13}$C($^1$H) NMR (151 MHz, C$_6$D$_6$): $\delta$ 186.86, 141.47, 133.31, 132.48, 132.02, 128.53, n. o. (BC).
B NMR (128 MHz, CD6D): δ 40.26.

7.1.4.11. *Synthesis of 137-Si*

A solution of 121 (0.408 g, 1.26 mmol) in THF (10 mL) was cooled to −78°C using an isopropanol-dry ice bath and nBuLi (2.5 M in "hexane, 0.504 mL, 1.26 mmol) was then added dropwise over 30 min. The completion of the lithiation reaction was verified by quenching a small volume of the reaction mixture with D2O, drying the organic phase with MgSO4 and analyzing it via GC-MS. A solution of 140 (0.3 g, 1.26 mmol) in THF (8 mL) was then added to the reaction and the solution stirred for 20 min at −78°C. The reaction was then removed from the cooling bath and allowed to reach room temperature. The solution was then quenched with a saturated NaHCO3 solution (30 mL) and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried over MgSO4, filtered, and the solvent was evaporated. The obtained crude material was then washed with a "hexane/ethyl acetate mixture. In the attempt of isolating compound 141, the obtained material was purified via chromatography separation ("hexane/MeOH gradient). However, under the described chromatographic conditions, compound 141 spontaneously converted to compound 137-Si which hindered the isolation of the tertiary alcohol and only fractions containing both compound or pure 137-Si were isolated. The mixed fractions were then dried, the obtained material was then dissolved in chloroform (30 mL) and molecular sieves were added. The solution was left for 16 h at r.t, the solvent was then separated from the molecular sieves and dried. Combining the obtained material with the pure fraction obtained via column chromatography yielded compound 137-Si in 58% yield (0.340 g, 0.73 mmol).

1H NMR (500 MHz, CDCl3): δ 7.72 (2H, t, J = 7.7 Hz), 7.61 (2H, dd, J = 7.3 Hz, J = 1.6 Hz), 7.58 (1H, ddt, J = 7.9 Hz, J = 7.1 Hz, J = 1.2 Hz), 7.51 (2H, dd, J = 8.4 Hz, J = 1.3 Hz), 7.35 (2H, d, J = 8.0 Hz), 7.23 (2H, ddd, J = 8.2 Hz, J = 7.1 Hz, J = 1.6 Hz), 7.15 (2H, td, J = 7.3 Hz, J = 1.1 Hz), 6.80 (2H, ddd, J = 8.4 Hz, J = 7.0 Hz, J = 1.8 Hz), 6.60 (2H, dd, J = 7.9 Hz, J = 1.7 Hz), 6.55 (2H, ddd, J = 7.8 Hz, J = 7.0 Hz, J = 1.2 Hz), 6.26 (2H, dd, J = 8.4 Hz, J = 1.1 Hz), 0.64 (6H, s).

13C{1H} NMR (126 MHz, CDCl3): δ 157.51, 141.47, 138.74, 134.32, 132.86, 132.31, 131.83, 131.60, 131.32, 130.18, 130.08, 128.57, 126.24, 124.98, 120.60, 114.55, 53.45, 0.47.
7.1.5. Synthesis of 37-OH and its derivatives

7.1.5.1. Synthesis of 37-OH

Method A – from 119-Cl

Mg(anthracene)\textperiodcentered 3THF (0.05 g, 0.105 mmol) was suspended in MTBE (5 mL) in a crimped vial and stirred at 75°C for 4 h. During this time, Mg\textsuperscript{4} was generated in-situ and the orange suspension turned into a grey metallic suspension. The mixture was let cooling to room temperature and a solution of diisopropylaminoborane (0.018 g, 0.160 mmol), and 119-Cl (0.05 g, 0.105 mmol) in MTBE (3 mL) was added through the septum with a syringe. The suspension was stirred at 45°C for 16 h, quenched with ice and the aqueous phase acidified using a 3 M HCl solution. Ethyl acetate (10 mL) was added, and the two phases separated, the aqueous phase was extracted with DCM (10 mL) and the combined organic phases were then dried over MgSO\textsubscript{4}, filtered, and the solvent was evaporated. The obtained crude material was suspended in absolute THF (3 mL) and ethanolamine was added (0.01 g, 0.160 mmol). The suspension was stirred for 16 h, the solid centrifuged down and washed with THF (2 \times 10 mL). The obtained ethanolamine adduct derivative was hydrolyzed by suspending the solid in a 3 M HCl solution (10 mL), adding DCM (10 mL) and stirring the heterogeneous mixture until all the solid dissolved. The organic phase was washed with a 3 M HCl solution (2 \times 10 mL), dried over MgSO\textsubscript{4}, filtered, and the solvent was evaporated. The product was obtained as a white powder containing 0.5 equivalent of DCM co-crystallized (0.022 g, 0.046 mmol, 44% yield).

Method B – from 135-OB

135-OB (0.262 g, 0.66 mmol) was dissolved in THF (33 mL) and cooled to -78°C using an isopropanol-dry ice bath. A solution of 127-Li \cdot Et\textsubscript{2}O in THF (10 mL) was added dropwise, the mixture was left slowly warm up to room temperature and stirred for 16 h. The solvent was evaporated, the solid suspended in diethylether (4 mL) and the mixture cooled with an ice bath. 3 M HCl in MCPE (1.76 mL, 5.28 mmol) was added dropwise and the suspension stirred at room temperature for 3.5 h. The reaction was quenched with a 3 M HCl solution, and the aqueous phase extracted with DCM (3 \times 30 mL). The combined organic phases were dried over MgSO\textsubscript{4}, filtered, and the solvent was evaporated. The obtained crude material was suspended in absolute THF (20 mL) and ethanolamine was added (0.201 g, 3.3 mmol). The suspension was stirred for 16 h, the solid centrifuged down and washed with a 1/1 THF/\textsuperscript{m}hexane mixture (2 \times 15 mL). The obtained ethanolamine adduct derivative was hydrolyzed by suspending the solid in a 3 M HCl solution (20 mL), adding DCM (30 mL) and stirring the heterogeneous mixture until all the solid dissolved. The organic phase was washed with a 3 M HCl solution (2 \times 20 mL), dried over MgSO\textsubscript{4}, filtered, and the
solvent was evaporated. The product was obtained as a white powder containing 1 equivalent of co-crystallized DCM (0.194 g, 0.37 mmol, 56% yield).

$^1$H NMR (600 MHz, DMSO-$d_6$): δ 10.11 (1H, s), 8.15 (2H, dd, $J = 7.5$ Hz, $J = 1.5$ Hz), 7.79 (2H, t, $J = 7.8$ Hz), 7.65 (1H, t, $J = 7.5$ Hz), 7.58 (2H, dd, $J = 8.3$ Hz, $J = 1.2$ Hz), 7.40 (2H, ddd, $J = 8.0$ Hz, $J = 7.1$ Hz, $J = 1.6$ Hz), 7.26 (2H, d, $J = 8.1$ Hz), 7.23 (2H, td, $J = 7.3$ Hz, $J = 1.0$ Hz), 6.82 (2H, ddd, $J = 8.6$ Hz, $J = 7.0$ Hz, $J = 1.6$ Hz), 6.50 (2H, ddd, $J = 7.7$ Hz, $J = 7.1$ Hz, $J = 1.2$ Hz), 6.31 (2H, dd, $J = 7.9$ Hz, $J = 1.5$ Hz), 6.16 (2H, dd, $J = 8.5$ Hz, $J = 1.0$).

$^{13}$C($^1$H) NMR (151 MHz, DMSO-$d_6$): δ 160.16, 140.54, 138.90, 132.38, 132.04, 131.44, 131.43, 130.96, 130.06, 129.72 (BC), 128.85, 128.8, 126.36, 124.83, 120.11, 114.19, 50.86.

$^{11}$B NMR (128 MHz, acetone-$d_6$): δ 38.73.

7.1.5.2.  **Synthesis of 37-F$_2$K**

37-OH (0.190 g, 0.44 mmol) and KHF$_2$ (0.273 g, 3.5 mmol) were loaded as solids in a plastic vessel, methanol (20 mL) was added, and the suspension stirred for 16 h. The solvent was dried under vacuum and the product was extracted with acetone ($3 \times 15$ mL, previously dried with MgSO$_4$ and filtered). The solvent was evaporated under vacuum and the obtained crude material washed with diethyl ether ($3 \times 5$ mL) (0.151 g, 0.30 mmol, 68% yield)

$^1$H NMR (500 MHz, acetone-$d_6$): δ 7.77 (2H, t, $J = 7.8$ Hz), 7.74 (2H, dd, $J = 7.1$ Hz, $J = 1.0$ Hz), 7.61 (1H, t, $J = 7.4$ Hz), 7.51 (2H, dd, $J = 8.2$ Hz, $J = 1.3$ Hz), 6.99 (2H, d, $J = 7.8$ Hz), 6.89 (2H, td, $J = 7.1$ Hz, $J = 1.4$ Hz), 6.85 (4H, m), 6.68 (2H, ddd, $J = 8.5$ Hz, $J = 7.0$ Hz, $J = 1.6$ Hz), 6.41 (2H, ddd, $J = 8.0$ Hz, $J = 7.2$ Hz, $J = 1.2$ Hz), 6.13 (2H, dd, $J = 8.4$ Hz, $J = 1.1$ Hz).

$^{13}$C($^1$H) NMR (151 MHz, acetone-$d_6$): δ 154.37, 141.26, 138.38, 132.57, 132.48, 130.54, 130.35, 130.17, 129.28, 127.17, 124.00, 123.95, 122.29, 118.45, 112.36, 50.35.

$^{19}$F NMR (376 MHz, acetone-$d_6$): δ -149.64.

$^{11}$B NMR (128 MHz, acetone-$d_6$): δ 3.67.
37-F$_2$K (0.151 g, 0.30 mmol) was suspended in chloroform (10 mL, stabilized with amylene) and a solution of trimethylsilyl chloride (0.163 g, 1.5 mmol) in chloroform (5 mL) was added dropwise and the mixture stirred for 2 h. The solvent and the excess trimethylsilyl chloride are thoroughly removed under vacuum and the residue is suspended in benzene (15 mL). To the mixture a suspension of mesityllithium (0.120 g, 0.6 mmol) in benzene (5 mL) is added and the mixture stirred for 16 h. The reaction mixture was quenched with water, the two phases separated, and the aqueous phase extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over MgSO$_4$, filtered, and the solvent was evaporated. The crude product was purified via column chromatography (n-hexane/ethyl acetate gradient, Rf = 0.63, n-hexane/ethyl acetate, 3: 1). The obtained off-white solid was dissolved in DCM and precipitated by adding n-hexane. The solid was separated via centrifugation and dried under vacuum. The analytically pure product was obtained as a white powder (0.037 g, 0.069 mmol, 23% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.73 (2H, t, $J$ = 7.7 Hz), 7.64 (2H, dd, $J$ = 7.5 Hz, $J$ = 1.4 Hz), 7.59 (1H, t, $J$ = 7.5 Hz), 7.54 (2H, d, $J$ = 7.6 Hz), 7.49 (2H, d, $J$ = 7.7 Hz), 7.44 (2H, ddd, $J$ = 8.0 Hz, $J$ = 7.0 Hz, $J$ = 1.5 Hz), 7.15 (2H, td, $J$ = 7.3 Hz, $J$ = 1.1 Hz), 7.00 (2H, s), 6.85 (2H, ddd, $J$ = 8.5 Hz, $J$ = 7.1 Hz, $J$ = 1.7 Hz), 6.53 (2H, t, $J$ = 7.5 Hz), 6.47 (2H, dd, $J$ = 7.8 Hz, $J$ = 1.6 Hz), 6.32 (2H, dd, $J$ = 8.4 Hz, $J$ = 0.7 Hz), 2.44 (3H, s), 2.18 (6H, s).

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 160.69, 141.34, 139.69, 138.42, 136.92, 136.91, 136.91, 134.41, 132.71, 131.62, 131.53, 131.36, 128.67, 128.65, 127.10, 126.67, 125.65, 120.57, 115.01, 52.67, 23.05, 21.49, n. o. (BC).

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ 35.16.
7.2. Photophysical measurements

7.2.1. Sample preparation

The PPMA (Sigma-Aldrich, MW = 120,000 g/mol) thin films of compounds 36, 50, 51, and 52, measured under standard atmospheric conditions, were prepared via spin coating technique according to the following procedure. A DCM solution (150 μL) containing the emitter and PMMA in concentration of 2.5 mg/gsolution and 50 mg/gsolution was spin coated on a quartz plate (2.5 cm × 2.5 cm) spinning at 100 rpm.

The PPMMA or ZEONEX® (Zeon Corporation, Zeonex 480) polymeric thin films of compounds 36, 53, 54, 55, 56, and 57, were kept under vacuum, and they were prepared according to the following procedure. A glass NRM tube was filled with at solution containing the emitter and the polymer in concentration of 4.5 mg/gsolution and 90 mg/gsolution, respectively. DCM or toluene were used as the solvent when PMMA or ZEONEX® were employed, respectively. The NMR tube was then emptied and the thin layer of solution that remained on the inner surface of the tube was dried under vacuum for 12 h. Finally, the NMR tube was flame sealed under vacuum.

For the solution measurements, UV-vis spectroscopic grade solvents were employed. For the measurements under degassed conditions, the solution containing the emitter was degassed by four freeze-pump-thaw cycles in a custom-made cuvette with a Teflon screw cap. The luminescence measurements were carried out on a PicoQuant FluoTime 300 spectrometer. A xenon lamp was utilized as the light source for steady-state photoluminescence measurements. For time-resolved measurements was used a pulsed LED (PicoQuant PLS 320) with λexc = 325 nm and pulse width of 600 ps, or a pulsed laser (LDH-P-C-405) with λexc = 405 nm and pulse width (FWHM) < 50 ps (for lifetimes < 20μs) or a pulsed xenon flash lamp with a pulse width of 400 ns. The second-order diffraction band was suppressed by employing a long-pass filters in the emission beam path. Absorption spectra were recorded on an HP 8453 UV-vis spectrophotometer.

7.2.2. Time-correlated single-photon counting (TCSPC) experiments

The long-lived emissions of the toluene solutions are unequivocally identified by the curve fit of the decays. In the cases where the signal of the pulsed source constituted a consisten portion of the transient decay the the pile-up rates were kept below 10% and the instrument response function (IRF) was utilized in the iterative deconvolution. For decays where the excitation of the pulsse constituted only a minimal parto of the decay, a tail-fit was performed and no IRF was taken into account.

7.3. Single-crystal X-ray crystallography

Suitable crystals were selected and mounted on MiTeGen Dual-Thickness MicroMounts in paraffin oil on a STOE IPDS 2T diffractometer equipped with a graphite-monochromated radiation source and an image plate detector. The crystals were kept at 100 K during data collection.The structures were solved with the ShelXS structure solution program9 using Direct Methods and refined with the ShelXL refinement package10 using Least Squares minimization within the software Olex211.
8. Bibliography

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C. Cui and F. Jakle, *Chemical Communications*, 2009, 2744-2746.


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9. Appendix

9.1. NMR spectra

NMR spectra of 37-OH

Fig. 183 $^1$H NMR spectrum of 37-OH.
Fig. 184 $^{13}$C($^1$H) NMR spectrum of 37-OH.

Fig. 185 $^{11}$B NMR spectrum of 37-OH.
NMR spectra of 37-F2K

Fig. 186 $^1$H NMR spectrum of 37-F2K.

Fig. 187 $^{13}$C($^1$H) NMR spectrum of 37-F2K.
Fig. 188 $^{11}$B NMR spectrum of 37-F2K.

Fig. 189 $^{19}$F NMR spectrum of 37-F2K.
NMR spectra of 37-Mes

Fig. 190 $^1H$ NMR spectrum of 37-Mes.

Fig. 191 $^{13}C(^1H)$ NMR spectrum of 37-Mes.
Fig. 192 $^{11}B$ NMR spectrum of $^{37}$Mes.

**NMR spectra of 40-Sn**

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Fig. 193 $^1H$ NMR spectrum of 40-Sn.
Fig. 194 $^{13}$C($^1$H) NMR spectrum of 40-Sn.

**NMR spectra of 36**

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Fig. 195 $^1$H NMR spectrum of 36.
Fig. 196 $^{13}$C(1H) NMR spectrum of 36.

Fig. 197 $^{11}$B NMR spectrum of 36.
NMR spectra of benzo[h]quinoline borane dibromide complex (44)

**Fig. 198** $^1$H NMR spectrum of benzo[h]quinoline borane dibromide complex 44.

**Fig. 199** $^{13}$C($^1$H) NMR spectrum of benzo[h]quinoline borane dibromide complex 44.
Fig. 200 $^{11}$B NMR spectrum of benzo[h]quinoline borane dibromide complex 44.

NMR spectra of 2-phenylbenzo[g]quinoline borane dibromide complex 45

Fig. 201 $^1$H NMR spectrum of 2-phenylbenzo[g]quinoline borane dibromide complex 45.
Fig. 202 $^{13}$C($^1$H) NMR spectrum of 2-phenylbenzo[g]quinoline borane dibromide complex 45.

Fig. 203 $^{11}$B NMR spectrum of 2-phenylbenzo[g]quinoline borane dibromide complex 45.
NMR spectra of 49

**Fig. 204** $^1$H NMR spectrum of 49.

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**Fig. 205** $^{13}$C($^1$H) NMR spectrum of 49.

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NMR spectra of 50

**Fig. 206** $^1$H NMR spectrum of 50

**Fig. 207** $^{13}$C($^1$H) NMR spectrum of 50
NMR spectra of 51

Parameters:
1. Solvent: CDC13
2. Spectrometer Frequency: 399.79 MHz
3. Nucleus: 1H
Fig. 210 $^{13}$C($^1$H) NMR spectrum of 51.

Fig. 211 $^{11}$B NMR spectrum of 51.
NMR spectra of 52

Fig. 212 $^1$H NMR spectrum of 52.

Fig. 213 $^{13}$C($^1$H) NMR spectrum of 52.
Fig. 214 $^{11}$B NMR spectrum of S2.

**Parameter** | **Value**
--- | ---
1 Solvent | CD$_2$Cl$_2$
2 Spectrometer Frequency | 128.27
3 Nucleus | 11B

Fig. 215 $^{19}$F NMR spectrum of S2.

**Parameter** | **Value**
--- | ---
1 Solvent | CD$_2$Cl$_2$
2 Spectrometer Frequency | 376.14
3 Nucleus | 19F
**NMR spectra of 53**

**Fig. 216** $^1H$ NMR spectrum of 53.

**Fig. 217** $^{13}C(^1H)$ NMR spectrum of 53.
NMR spectra of 54

- **Solvent**: CDCl₃
- **Spectrometer Frequency**: 400.13 MHz
- **Nucleus**: 1H

Fig. 219 ¹H NMR spectrum of 54.
Fig. 220 $^{13}$C(1H) NMR spectrum of 54.

Fig. 221 $^{11}$B NMR spectrum of 54.
**NMR spectra of 55**

![1H NMR spectrum of 55.](image1)

![13C{1H} NMR spectrum of 55.](image2)

---

*Fig. 222 ¹H NMR spectrum of 55.*

*Fig. 223 ¹³C{¹H} NMR spectrum of 55.*
Fig. 224 $^1$B NMR spectrum of 55.

**NMR spectra of 56**

![NMR spectrum of 56](image)

Fig. 225 1H NMR spectrum of 56.
Fig. 226 $^{13}$C($^1$H) NMR spectrum of S6.

Fig. 227 $^{11}$B NMR spectrum of S6.
NMR spectra of 57

**Fig. 228** $^1$H NMR spectrum of 57.

**Parameter** | **Value**
--- | ---
1. Solvent | CDC3
2. Spectrometer Frequency | 400.13
3. Nucleus | 1H

**Fig. 229** $^{13}$C($^1$H) NMR spectrum of 57.

**Parameter** | **Value**
--- | ---
1. Solvent | CDC3
2. Spectrometer Frequency | 201.26
3. Nucleus | 13C
Fig. 230 $^{11}$B NMR spectrum of 57.

NMR spectra of En-59

Fig. 231 $^1$H NMR spectrum of En-59.
Fig. 232 $^{13}$C($^1$H) NMR spectrum of En-59.

Fig. 233 $^{11}$B NMR spectrum of En-59.
NMR spectra of 60

Fig. 234 $^1$H NMR spectrum of 60.

Fig. 235 $^{13}$C($^1$H) NMR spectrum of 60.
NMR spectra of Di-65

Fig. 236 $^1$H NMR spectrum of Di-65.

Fig. 237 $^{13}$C($^1$H) NMR spectrum of Di-65.
**NMR spectra of Di-65**

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*Fig. 238 $^{11}$B NMR spectrum of Di-65.*

**NMR spectra of En-69**

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*Fig. 239 $^1$H NMR spectrum of En-69.*
**Fig. 240** \(^{13}\text{C}\)\(^{1}(H)\) NMR spectrum of \textit{En}-69.

**Fig. 241** \(^{11}\text{B}\) NMR spectrum of \textit{En}-69.
NMR spectra of En-71

**Fig. 242** $^1$H NMR spectrum of En-71.

**Fig. 243** $^{13}$C($^1$H) NMR spectrum of En-71.
**Fig. 244** $^{11}$B NMR spectrum of En-71.

**Fig. 245** $^{19}$F NMR spectrum of En-71.
NMR spectra of En-76-trans

Fig. 246 $^1$H NMR spectrum of En-76-trans.

Fig. 247 $^{11}$B NMR spectrum of En-76-trans.
Fig. 248 $^{31}$P NMR spectrum of En-76-trans.

**NMR spectra of B3**

Fig. 249 $^1$H NMR spectrum of B3.
Fig. 250 $^{13}$C($^1$H) NMR spectrum of 83.

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Fig. 251 $^{11}$B NMR spectrum of 83.

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NMR spectra of $^{119}$Cl

Fig. 252 $^1$H NMR spectrum of $^{119}$Cl.

Fig. 253 $^{13}$C($^1$H) NMR spectrum of $^{119}$Cl.
NMR spectra of **$^{127}$Li$\cdot$Et$_2$O**

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Fig. 254 $^1$H NMR spectrum of **$^{127}$Li$\cdot$Et$_2$O**.

NMR spectra of **$^{124}$Cl**

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Fig. 255 $^1$H NMR spectrum of **$^{124}$Cl**.
**Fig. 256** $^{13}$C($^1$H) NMR spectrum of 124-Cl.

**NMR spectra of 134-OH**

**Fig. 257** $^1$H NMR spectrum of 134-OH.
Fig. 258 $^{13}$C($^1$H) NMR spectrum of $^{134}$-OH.

Fig. 259 $^{11}$B NMR spectrum of $^{134}$-OH.
NMR spectra of \textbf{134-DMEA}

\begin{itemize}
  \item Fig. 260 $^1$H NMR spectrum of \textbf{134-DMEA}.
  \item Fig. 261 $^{13}$C($^1$H) NMR spectrum of \textbf{134-DMEA}
\end{itemize}
NMR spectra of 135-OH

Fig. 262 $^{11}$B NMR spectrum of 134-DMEA

Fig. 263 $^1$H NMR spectrum of 135-OH.
Fig. 264 $^{13}$C($^1$H) NMR spectrum of 135-OH.

Fig. 265 $^{11}$B NMR spectrum of 135-OH.
NMR spectra of 135-OB

**Fig. 266** $^1$H NMR spectrum of 135-OB.

**Fig. 267** $^{13}$C($^1$H) NMR spectrum of 135-OB.
**Fig. 268** $^{11}$B NMR spectrum of $^{135}$OB.

**NMR spectra of $^{137}$Si**

**Fig. 269** $^1$H NMR spectrum of $^{137}$Si.
Fig. 270 $^{13}$C({H}) NMR spectrum of \textit{137-Si}. 
9.2. TCSPC decay curves

Fig. 271 Transient decay of 36 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Fig. 272 Transient decay of 36 embedded in PMMA polymeric thin film spincoated on quartz plate (emitter concentration 5%). Pulsed source: diode emitting at 320 nm. Decay curves deconvoluted using a two exponential function (left) or a three exponential function (right).
Transient decay of 50

Fig. 273 Transient decay of 50 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Fig. 274 Transient decay of 50 embedded in PMMA polymeric thin film spincasted on quartz plate (emitter concentration 5%). Pulsed source: diode emitting at 320 nm. Decay deconvoluted using a two exponential function.
Transient decay of $^{51}$

Fig. 275 Transient decay of $^{51}$ in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Fig. 276 Transient decay of $^{51}$ embedded in PMMA polymeric thin film spincasted on quartz plate (emitter concentration 5%). Pulsed source: flash lamp, selected wavelength: 330 nm. Decay deconvoluted using a two exponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a two exponential function (right).
Fig. 277 Transient decay of $\text{S}1$ embedded in PMMA polymeric thin film kept under vacuum in a sealed NMR tube. (concentration 5%). Pulsed source flash lamp, selected wavelength: 330 nm. Decay interpolated by performing a tail fit with a biexponential function.

Fig. 278 Transient decay of $\text{S}1$ embedded in ZEONEX® polymeric thin film kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source: flash lamp, selected wavelength: 330 nm. Decay deconvoluted using a two exponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a two exponential function (right).
Fig. 279 Transient decay of 51 embedded in ZEONEX® polymeric thin film kept under vacuum in a sealed NMR tube (concentration 5%). Pulsed source: diode emitting at 320 nm. Decay deconvoluted using a two exponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a two exponential function (right).

Transient decay of 52

![Graphs showing transient decay of 52 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.](image)

Fig. 280 Transient decay of 52 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.
Fig. 281 Transient decay of 50 embedded in PMMA polymeric thin film spincasted on quartz plate (emitter concentration 5%). Pulsed source: diode emitting at 320 nm. Decay deconvoluted using a two exponential function.

Transient decay of 53

Fig. 282 Transient decay of 53 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.
Fig. 283 Transient decay of $^{53}$Zn embedded in PMMA polymeric thin film kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source flash lamp, selected wavelength: 370 nm. Decay interpolated by performing a tail fit with a biexponential function.

Fig. 284 Transient decay of $^{53}$Zn embedded in PMMA polymeric thin film kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source flash lamp, selected wavelength: 370 nm. Decay deconvoluted using a biexponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a biexponential function (right).
Transient decay of $^{54}$

Fig. 285 Transient decay of $^{54}$ in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Fig. 286 Transient decay of $^{54}$ embedded in PMMA polymeric thin film (left) or ZEONEX® thin film (right). Both thin films were kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source: diode emitting at 320 nm. Decays deconvoluted using a monoexponential function and taking into account the instrument IRF.
Transient decay of 55

Fig. 287 Transient decay of 55 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm (left), flash lamp (right) selected wavelength: 320 nm.

Fig. 288 Transient decay of 55 embedded in PMMA polymeric thin film (left) or ZEONEX® thin film (right). Both thin films were kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source: flash lamp, selected wavelength: 370 nm. Decays interpolated by performing a tail fit with a biexponential function.
Transient decay of 56

Fig. 289 Transient decay of 56 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Fig. 290 Transient decay of 56 embedded in PMMA polymeric thin film kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source flash lamp, selected wavelength: 370 nm. Decay deconvoluted using a biexponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a biexponential function (right).
Fig. 291 Transient decay of 56 embedded in ZEONEX® polymeric thin film kept under vacuum in a sealed NMR tube (emitter concentration 5%). Pulsed source flash lamp, selected wavelength: 370 nm. Decay deconvoluted using a biexponential function and taking into account the instrument IRF and (left) or interpolated by performing a tail fit with a biexponential function (right).

Fig. 292 Transient decay of 56 embedded in ZEONEX® polymeric thin film kept under vacuum in a sealed NMR tube (concentration 5%). Pulsed source: diode emitting at 320 nm. Decay interpolated by performing a tail fit with a two exponential function.
Transient decay of **57**

![Graph](image)

Fig. 293 Transient decay of **57** in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: laser emitting at 405 nm.

**Transient decay of En-59**

![Graph](image)

Fig. 294 Transient decay of **En-59** in toluene solution in the presence of air. Pulsed source: diode emitting at 320 nm.
Fig. 295 Transient decay of En-59 in toluene solution in the absence of air. Pulsed source: diode emitting at 320 nm (left), flash lamp, selected wavelength: 320 nm (right).

Transient decay of Di-65

Fig. 296 Transient decay of Di-65 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.
Transient decay of En-69

![Graph of transient decay of En-69](image)

Fig. 297 Transient decay of En-69 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.

Transient decay of En-71

![Graph of transient decay of En-71](image)

Fig. 298 Transient decay of En-71 in toluene solution in the presence of air (left) and absence of air (right). Pulsed source: diode emitting at 320 nm.
Fig. 299 Transient decay of En-71 embedded in ZEONEX® polymeric thin film kept under vacuum in a sealed NMR tube (concentration 5%). Pulsed source: diode emitting at 320 nm. Decay interpolated by performing a tail fit with a two exponential function.
9.3. Single-crystal X-ray crystallography

9.3.1. tables

<table>
<thead>
<tr>
<th>Compound</th>
<th>37-OH · CHCl₃</th>
<th>37-Mes</th>
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<th>43</th>
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<td>Chemical formula</td>
<td>C₃₁H₂₂BNO · CHCl₃</td>
<td>C₃₆H₃₂BN</td>
<td>C₄₀H₃₂BN₂</td>
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<td>MW [g mol⁻¹]</td>
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<td>P2₁/c</td>
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<td>a [Å]</td>
<td>9.3869(10)</td>
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<td>10.4501(8)</td>
<td>7.0117(4)</td>
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<td>c [Å]</td>
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<td>17.7772(6)</td>
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<td>β [°]</td>
<td>91.576(9)</td>
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<td>V [Å³]</td>
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<td>2Θ range for data collection [°]</td>
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<td>5.562 to 57.112</td>
<td>5.132 to 59.136</td>
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<td>Index ranges</td>
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<td>Reflections collected</td>
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<td>No. of independent reflections (Rint, R̃int)</td>
<td>5004 (0.0534, 0.0495)</td>
<td>8643 (0.0450, 0.0446)</td>
<td>4527 (0.0510, 0.0496)</td>
<td>3706 (0.0503, 0.0259)</td>
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<td>8643/0/382</td>
<td>4527/2/245</td>
<td>3706/0/174</td>
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<td>Goodness-of-fit on F²</td>
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<td>R₁, wR₁ (I ≥ 2σ(I))</td>
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<td>R₁, wR₁ (all data)</td>
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<td>0.0616, 0.0966</td>
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<td>Largest diff. peak/hole [e Å⁻³]</td>
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<td>Flack parameter</td>
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*Table 21 Crystallographic data for 37-OH, 37-Mes, 36 and 43.*
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<tr>
<th>Compound</th>
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<th>50 - 0.5 CH₂Cl₂</th>
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<td>100</td>
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<td>monoclinic</td>
<td>triclinic</td>
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<td>P2₁</td>
<td>P-1</td>
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<td>α [Å]</td>
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<td>8.6076(3)</td>
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<td>c [Å]</td>
<td>10.0715(10)</td>
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<td>10.5865(7)</td>
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<td>ρ_calcd [g cm⁻³]</td>
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<td>μ [mm⁻¹]</td>
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<td>2θ range for data collection [°]</td>
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<td>Reflections collected</td>
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<td>R₁, wR₂ (I ≥ 2σ(I))</td>
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*Table 22 Crystallographic data for 44, 50, 51 and 52.*
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<td>100(1)</td>
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<td>P-1</td>
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<td>90</td>
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<td>0.075</td>
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<td>832.0</td>
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<td>0.35 × 0.15 × 0.1</td>
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<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
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<td>4.722 to 57.132</td>
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<td>-11 ≤ l ≤ 10, -22 ≤ l ≤ 22, -22 ≤ l ≤ 26, -18 ≤ l ≤ 18,</td>
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<td>No. of independent reflections (R_{int}, R_{sigma})</td>
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<td>9812 (0.0324, 0.0372)</td>
<td>4603 (0.0369, 0.0289)</td>
<td>9302 (0.0410, 0.0540)</td>
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<td>9812/245/769</td>
<td>4603/0/254</td>
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<td>Goodness-of-fit on F²</td>
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<td>1.180</td>
<td>1.045</td>
<td>1.039</td>
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<td>R₁, wR₂ (I ≥ 2σ(I))</td>
<td>0.0412, 0.0957</td>
<td>0.0617, 0.1174</td>
<td>0.0372, 0.0930</td>
<td>0.0611, 0.1469</td>
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<td>R₁, wR₂ (all data)</td>
<td>0.0674, 0.1098</td>
<td>0.0822, 0.1231</td>
<td>0.0524, 0.0981</td>
<td>0.0860, 0.1575</td>
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<td>Largest diff. peak/hole [e Å⁻³]</td>
<td>0.31/-0.21</td>
<td>0.28/-0.23</td>
<td>0.41/-0.31</td>
<td>0.74/-0.47</td>
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<td>Flack parameter</td>
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Table 23 Crystallographic data for 53, 54, 55 and 56.
<table>
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<tr>
<th>Compound</th>
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<th>En-59</th>
<th>Di-65</th>
<th>En-69 · CH₂Cl₂</th>
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<tr>
<td>Chemical formula</td>
<td>C₁₁H₁₀BNS</td>
<td>C₁₂H₁₂BBrNS</td>
<td>C₁₇H₁₃B₂NO₂S</td>
<td>C₁₇H₂₄BNS · CH₂Cl₂</td>
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<tr>
<td>MW [g mol⁻¹]</td>
<td>449.35</td>
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<td>100(1)</td>
<td>100(1)</td>
<td>100(1)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁</td>
<td>P₂₁/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>9.2875(4)</td>
<td>14.6215(5)</td>
<td>8.5692(3)</td>
<td>17.3003(5)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>11.2138(3)</td>
<td>10.5049(3)</td>
<td>8.9852(3)</td>
<td>8.3154(4)</td>
</tr>
<tr>
<td>α [°]</td>
<td>90</td>
<td>90</td>
<td>89.880(3)</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>97.126(3)</td>
<td>113.774(3)</td>
<td>76.194(3)</td>
<td>105.605(2)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90</td>
<td>90</td>
<td>69.660(3)</td>
<td>90</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>2193.54(15)</td>
<td>2073.61(12)</td>
<td>738.32(5)</td>
<td>2873.90(18)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>ρcalcd [g cm⁻³]</td>
<td>1.361</td>
<td>1.532</td>
<td>1.298</td>
<td>1.364</td>
</tr>
<tr>
<td>μ [mm⁻¹]</td>
<td>0.169</td>
<td>2.099</td>
<td>0.146</td>
<td>0.329</td>
</tr>
<tr>
<td>F(000)</td>
<td>936.0</td>
<td>968.0</td>
<td>304.0</td>
<td>1224.0</td>
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<td>Crystal size [mm³]</td>
<td>0.5 × 0.3 × 0.25</td>
<td>0.2 × 0.15 × 0.075</td>
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</tr>
<tr>
<td>Radiation type</td>
<td>MoKα (λ = 0.71073)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2θ range for data collection [°]</td>
<td>5.04 to 59.138</td>
<td>4.914 to 52.238</td>
<td>5.722 to 59.062</td>
<td>6.068 to 59.296</td>
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<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -29 ≤ l ≤ 29</td>
<td>-18 ≤ h ≤ 18, -12 ≤ k ≤ 12, -17 ≤ l ≤ 18</td>
<td>-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14</td>
<td>-23 ≤ h ≤ 23, -11 ≤ k ≤ 10, -28 ≤ l ≤ 26</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>21123</td>
<td>24838</td>
<td>22788</td>
<td>21135</td>
</tr>
<tr>
<td>No. of independent reflections (Rint, Rsigma)</td>
<td>6126 [Rint = 0.0279, Rsigma = 0.0270]</td>
<td>4091 (0.0484, 0.0303)</td>
<td>7804 (0.0357, 0.0305)</td>
<td>8004 (0.0359, 0.0355)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>6126/0/308</td>
<td>4091/76/404</td>
<td>7804/3/392</td>
<td>8004/16/411</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.018</td>
<td>1.069</td>
<td>1.142</td>
<td>1.059</td>
</tr>
<tr>
<td>R₁, wR₁ (I ≥ 2σ(I))</td>
<td>0.0355, 0.0873</td>
<td>0.0530, 0.1205</td>
<td>0.0478, 0.1273</td>
<td>0.0464, 0.1268</td>
</tr>
<tr>
<td>R₁, wR₁ (all data)</td>
<td>0.0485, 0.0912</td>
<td>0.0669, 0.1271</td>
<td>0.0509, 0.1285</td>
<td>0.0672, 0.1374</td>
</tr>
<tr>
<td>Largest diff. peak/hole [e Å⁻³]</td>
<td>0.35/-0.30</td>
<td>1.54/-0.75</td>
<td>0.68/-0.33</td>
<td>0.54/-0.64</td>
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<td>Flack parameter</td>
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<td>-</td>
<td>0.01(2)</td>
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Table 24 Crystallographic data for 57, En-59, Di-65 and En-69.
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<tr>
<th>Compound</th>
<th>En-76-trans</th>
<th>77</th>
<th>159</th>
<th>121</th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{39}H_{47}BBrNP_{2}PtS</td>
<td>C_{25}H_{16}BNOS</td>
<td>C_{25}H_{19}BN_{2}S</td>
<td>C_{18}H_{14}BrN</td>
</tr>
<tr>
<td>MW [g mol^{-1}]</td>
<td>909.58</td>
<td>389.26</td>
<td>426.32</td>
<td>324.21</td>
</tr>
<tr>
<td>T [K]</td>
<td>100(1)</td>
<td>100(1)</td>
<td>100(1)</td>
<td>100</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>triclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P2_{1}/n</td>
<td>P-1</td>
</tr>
<tr>
<td>a [Å]</td>
<td>10.4437(2)</td>
<td>10.6303(4)</td>
<td>11.2585(4)</td>
<td>9.2240(10)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>12.3248(3)</td>
<td>11.7522(5)</td>
<td>15.2075(5)</td>
<td>10.0861(11)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>15.9281(4)</td>
<td>11.2585(4)</td>
<td>15.2075(5)</td>
<td>10.0861(11)</td>
</tr>
<tr>
<td>α [°]</td>
<td>110.982(2)</td>
<td>110.619(3)</td>
<td>90</td>
<td>83.253(9)</td>
</tr>
<tr>
<td>β [°]</td>
<td>96.249(2)</td>
<td>101.731(3)</td>
<td>99.691(2)</td>
<td>80.448(9)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>92.371(2)</td>
<td>104.158(3)</td>
<td>90</td>
<td>62.165(8)</td>
</tr>
<tr>
<td>V [Å^3]</td>
<td>1895.75(8)</td>
<td>930.27(7)</td>
<td>2158.44(13)</td>
<td>727.62(15)</td>
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<td>Z</td>
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<td>4</td>
<td>2</td>
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<td>µ_{calc} [g cm^{-3}]</td>
<td>1.593</td>
<td>1.390</td>
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<td>1.480</td>
</tr>
<tr>
<td>µ [mm^{-1}]</td>
<td>4.922</td>
<td>0.191</td>
<td>0.169</td>
<td>2.813</td>
</tr>
<tr>
<td>F(000)</td>
<td>904.0</td>
<td>404.0</td>
<td>888.0</td>
<td>328.0</td>
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<tr>
<td>Crystal size [mm^3]</td>
<td>0.35 × 0.2 × 0.1</td>
<td>0.5 × 0.4 × 0.15</td>
<td>0.35 × 0.3 × 0.2</td>
<td>0.3 × 0.15 × 0.075</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα (λ = 0.71073)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Θ range for data collection [°]</td>
<td>4.502 to 57.328</td>
<td>5.12 to 61.238</td>
<td>5.288 to 64.038</td>
<td>5 to 51.714</td>
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<tr>
<td>Index ranges</td>
<td>-14 ≤ h ≤ 14, -12 ≤ h ≤ 11, -19 ≤ h ≤ 17, -10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -15 ≤ k ≤ 15, -16 ≤ k ≤ 16, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21, -16 ≤ l ≤ 16, -22 ≤ l ≤ 22, -12 ≤ l ≤ 12</td>
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</tr>
<tr>
<td>Reflections collected</td>
<td>53663</td>
<td>23215</td>
<td>27675</td>
<td>11306</td>
</tr>
<tr>
<td>No. of independent reflections (R_{int}, R_{sigma})</td>
<td>9634 (0.0410, 0.0219)</td>
<td>5693 (0.0337, 0.0221)</td>
<td>7446 (0.0499, 0.0367)</td>
<td>2802 (0.0908, 0.0564)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>9634/35/514</td>
<td>5693/0/263</td>
<td>7446/0/289</td>
<td>2802/0/181</td>
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<td>Goodness-of-fit on F^2</td>
<td>1.046</td>
<td>1.060</td>
<td>1.056</td>
<td>1.005</td>
</tr>
<tr>
<td>R_{1}, wR_{2} (I ≥ 2σ(I))</td>
<td>0.0252, 0.0583</td>
<td>0.0383, 0.1033</td>
<td>0.0383, 0.0977</td>
<td>0.0420, 0.0980</td>
</tr>
<tr>
<td>R_{1}, wR_{2} (all data)</td>
<td>0.0309, 0.0602</td>
<td>0.0470, 0.1079</td>
<td>0.0563, 0.1043</td>
<td>0.0536, 0.1039</td>
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<td>Largest diff. peak/hole [e Å^{-3}]</td>
<td>0.84/-1.76</td>
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<td>0.43/-0.32</td>
<td>0.47/-0.87</td>
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<tr>
<td>Flack parameter</td>
<td>-</td>
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<td>-</td>
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*Table 25 Crystallographic data for En-76-trans, 77, 159 and 121.*
<table>
<thead>
<tr>
<th>Compound</th>
<th>135-OHQ · CHCl₃</th>
<th>137-Si</th>
<th>147 · BBr₃</th>
<th>151 · MeOH · CH₂Cl₂</th>
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</thead>
<tbody>
<tr>
<td><strong>Chemical formula</strong></td>
<td>C_{22}H_{14}BNO₂ · CHCl₃</td>
<td>C_{33}H_{14}NSi</td>
<td>C_{33}H_{14}BBr₂NSi · BBr₃</td>
<td>C_{34}H_{16}BN₂O₂ · CH₂O · CH₂Cl₂</td>
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<td><strong>MW [g mol⁻¹]</strong></td>
<td>454.52</td>
<td>465.64</td>
<td>2006.58</td>
<td>627.38</td>
</tr>
<tr>
<td><strong>T [K]</strong></td>
<td>100(1)</td>
<td>100(1)</td>
<td>100(1)</td>
<td>100(1)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P₂₁/n</td>
<td>P-1</td>
<td>P₂₁/c</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>9.5613(4)</td>
<td>10.6517(6)</td>
<td>15.5218(6)</td>
<td>8.8989(4)</td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>19.8246(6)</td>
<td>11.0821(7)</td>
<td>17.7452(5)</td>
<td>10.1400(5)</td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>10.6777(5)</td>
<td>11.6240(7)</td>
<td>26.2473(9)</td>
<td>18.5936(9)</td>
</tr>
<tr>
<td><strong>α [°]</strong></td>
<td>90</td>
<td>88.688(5)</td>
<td>90</td>
<td>84.679(4)</td>
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<tr>
<td><strong>β [°]</strong></td>
<td>96.189(4)</td>
<td>65.602(4)</td>
<td>93.367(3)</td>
<td>77.899(4)</td>
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<tr>
<td><strong>γ [°]</strong></td>
<td>90</td>
<td>88.795(5)</td>
<td>90</td>
<td>71.053(3)</td>
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<tr>
<td><strong>V [Å³]</strong></td>
<td>2012.15(14)</td>
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<td>7217.0(4)</td>
<td>1551.07(13)</td>
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<td><strong>Z</strong></td>
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<td>2</td>
<td>4</td>
<td>2</td>
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<tr>
<td><strong>ρ calculated [g cm⁻³]</strong></td>
<td>1.500</td>
<td>1.238</td>
<td>1.847</td>
<td>1.343</td>
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<tr>
<td><strong>μ [mm⁻¹]</strong></td>
<td>0.477</td>
<td>0.116</td>
<td>7.287</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>928.0</td>
<td>492.0</td>
<td>3864.0</td>
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<td><strong>Crystal size [mm³]</strong></td>
<td>0.4 × 0.15 × 0.1</td>
<td>0.15 × 0.1 × 0.05</td>
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</tr>
<tr>
<td><strong>Radiation type</strong></td>
<td>MoKα (λ = 0.71073)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2θ range for data collection [°]</strong></td>
<td>4.352 to 58.17</td>
<td>5.282 to 55.2</td>
<td>5.258 to 50.18</td>
<td>4.482 to 59.264</td>
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<td><strong>Index ranges</strong></td>
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<td>-12 ≤ h ≤ 13,</td>
<td>-18 ≤ h ≤ 18,</td>
<td>-12 ≤ h ≤ 12,</td>
</tr>
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<td><strong>Reflections collected</strong></td>
<td>22825</td>
<td>11831</td>
<td>37894</td>
<td>24742</td>
</tr>
<tr>
<td><strong>No. of independent reflections (R(int), Rσ) (all data)</strong></td>
<td>5364 (0.0358, 0.0285)</td>
<td>5724 (0.0485, 0.0710)</td>
<td>12697 (0.1000, 0.0447)</td>
<td>8655 (0.0447, 0.0285)</td>
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<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.017</td>
<td>1.009</td>
<td>0.966</td>
<td>1.024</td>
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<td><strong>R₁, wR₂ (I ≥ 2σ(I))</strong></td>
<td>0.0369, 0.0833</td>
<td>0.0492, 0.0940</td>
<td>0.0607, 0.1130</td>
<td>0.0421, 0.0983</td>
</tr>
<tr>
<td><strong>R₁, wR₂ (all data)</strong></td>
<td>0.0529, 0.0880</td>
<td>0.0873, 0.1056</td>
<td>0.1185, 0.1319</td>
<td>0.0603, 0.1044</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole [e Å⁻³]</strong></td>
<td>0.32/-0.35</td>
<td>0.33/-0.24</td>
<td>0.79/-1.22</td>
<td>0.39/-0.30</td>
</tr>
<tr>
<td><strong>Flack parameter</strong></td>
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<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

*Table 26 Crystallographic data for 135-OHQ, 137-Si, 147, and 151.*
9.3.2. Pictures of the solid state structures

Fig. 300 Solid-state structure of 37-OH ⋅ CHCl₃. The CHCl₃ molecule is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 301 Solid-state structure of 37-Mes. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 302 Solid-state structure of 36. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 303 Solid-state structure of 43. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 304 Solid-state structure of 44. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 305 Solid-state structure of 50 · 0.5 CH₂Cl₂. The CH₂Cl₂ molecule is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 306 Solid-state structure of 51. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 307 Solid-state structure of 52. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 308 Solid-state structure of 53. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 309 Solid-state structure of 54. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 310 Solid-state structure of 55. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 311 Solid-state structure of 56. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 312 Solid-state structure of 57. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 313 Solid-state structure of En-59. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 314 Solid-state structure of Di-65. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 315 Solid-state structure of En-69·CH$_3$Cl$_2$. The CH$_3$Cl$_2$ molecule is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 316 Solid-state structure of En-76-trans. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 317 Solid-state structure of 77. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 318 Solid-state structure of 159. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 319 Solid-state structure of 121. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 320 Solid-state structure of $\text{135-OHQ} \cdot \text{CHCl}_3$. The CHCl$_3$ molecule is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 321 Solid-state structure of $\text{137-Si}$. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 322 Solid-state structure of 147·BBr₃. The BBr₃ molecule is omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 323 Solid-state structure of 151 · MeOH · CH₂Cl₂. The MeOH and CH₂Cl₂ molecule are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.
### 9.4. Additional tables

<table>
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<tr>
<th>Compound</th>
<th>$^1$H NMR δ of CH₃ (ppm)</th>
<th>Solvent</th>
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</thead>
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<tr>
<td>Si(CH₃)₃Br</td>
<td>0.31⁴⁷³</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>Si(CH₃)₃Br</td>
<td>0.59⁴⁷⁴</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>Si(CH₃)₂Br₂</td>
<td>0.67⁴⁷³</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>Si(CH₃)₂Br₂</td>
<td>1.02⁴⁷⁵</td>
<td>Neat</td>
</tr>
<tr>
<td>Si(CH₃)Br</td>
<td>1.00⁴⁷³</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>Si(CH₃)₂Ph₂</td>
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<td>CDCl₃</td>
</tr>
<tr>
<td>Si(CH₃)₂PhBr</td>
<td>0.84⁴⁷⁷</td>
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<td>Si(CH₃)PhBr₂</td>
<td>1.33⁴⁷⁷</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>B(CH₃)Br₂</td>
<td>0.97⁴⁷⁵</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>B(CH₃)Br₂</td>
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</tr>
<tr>
<td>B(CH₃)Br₂</td>
<td>1.50⁴⁷⁹</td>
<td>Neat</td>
</tr>
<tr>
<td>B(CH₃)BrI</td>
<td>1.85⁴⁷⁹</td>
<td>Neat</td>
</tr>
<tr>
<td>B(CH₃)I₂</td>
<td>2.15⁴⁷⁹</td>
<td>Neat</td>
</tr>
</tbody>
</table>

$[1,1'$-Binaphthyl]-2,2'-diylbis[dimethylbromosilane] 0.01 and 0.04⁴⁸⁰ CCl₄

Table 27: Selected examples used as reference for the interpretation of the outcome delivered by the silicon-boron exchange reactions. The reported values refers to the shift recorded in the $^1$H NMR spectrum for the methyl group of the reported compounds.
<table>
<thead>
<tr>
<th>Compound</th>
<th>δ ¹H CH₃ (ppm)</th>
<th>J¹¹²/¹¹⁵Sn-H (Hz)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂Sn</td>
<td>0.07₄⁸₁</td>
<td>53.10/55.80₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>52/54.₃₄⁸²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-54.0₃⁴₅</td>
<td>CCl₄</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-53.₈₃⁴₅</td>
<td>benzene</td>
</tr>
<tr>
<td>Me₂SnCl</td>
<td>0.69₄⁸₁</td>
<td>57.22/59.₈₅₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>56/58.₅₄⁸²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-58.₁₃⁴₅</td>
<td>CCl₄</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-59.ₐ₃⁴₅</td>
<td>benzene</td>
</tr>
<tr>
<td>Me₂SnBr</td>
<td>0.7₉₄⁸₁</td>
<td>56.₇₀/5₉.₁₀₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>56/5₸.₅₄⁸²</td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-5₇.₈₃⁴₅</td>
<td>CCl₄</td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-5₮.₂₃⁴₅</td>
<td>benzene</td>
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<tr>
<td>Me₂SnI</td>
<td>0.₉₂₄⁸₁</td>
<td>₅₵.₉₅/₅₸.₆₅₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>5₶/₅₸.₅₄⁸²</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl₂</td>
<td>1.₂₃₄⁸₁</td>
<td>₆₆.₈₂/₆₉.₈₂₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₆₷/₇₀₄⁸₂</td>
<td></td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-₆₸.₂₃⁴₅</td>
<td>CCl₄</td>
</tr>
<tr>
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<td>-₆₹.₀₃⁴₅</td>
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<tr>
<td>Me₂SnBr₂</td>
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<td>₆₵.₇₀/₆₸.₉₂₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₆₳/₆₶.₄₄₈²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-₆₶.₇₃⁴₅</td>
<td>CCl₄</td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-₆₷.₀₃⁴₅</td>
<td>benzene</td>
</tr>
<tr>
<td>Me₂SnI₂</td>
<td>1.₆₉₄⁸₁</td>
<td>₆₁.₉₅/₆₄.₅₀₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₆₀/₆₂.₅₄⁸²</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl₃</td>
<td>1.₇₁₄⁸₁</td>
<td>₉₇.₇₂/₁₀₁.₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₉₵.₅/₉₸.₄₄₈²</td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-₹₸.₇₃⁴₅</td>
<td>CCl₄</td>
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<tr>
<td></td>
<td>ₐ</td>
<td>-₹₹.₉₃⁴₅</td>
<td>benzene</td>
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<tr>
<td>Me₂SnBr₃</td>
<td>1.₉₀₄⁸₁</td>
<td>₈₶.₄₀/₉₀.₁₈₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₈₵/₈₉₄₸²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>-₸₸.₅₃⁴₅</td>
<td>CCl₄</td>
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<tr>
<td></td>
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<td>-₸₸.₉₃⁴₅</td>
<td>benzene</td>
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<tr>
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<td>2.₃₇₄⁸₁</td>
<td>₇₂.₉₀/₇₆.₂₀₄⁸₁</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>ₐ</td>
<td>₇₀/₇₃₄⁸₂</td>
<td></td>
</tr>
<tr>
<td>Me₃PhSn</td>
<td>ₐ</td>
<td>₅₴.₆₄₈²</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>Me₃Ph₂Sn</td>
<td>₀.₄₆₄⁸₁</td>
<td>₅₴.₂₂/₅₷.₃₀₄⁸₁</td>
<td>CDCl₃</td>
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<tr>
<td>Me₃PhSnCl</td>
<td>ₐ</td>
<td>-₵₸.₅₄₈⁴</td>
<td>C₆D₆</td>
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<td>₅₴.₀₂/₅₷.₀₀₄⁸₁</td>
<td>CDCl₃</td>
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<tr>
<td>Me₃Ph₂SnCl</td>
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<tr>
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<td>₀.₈₈₄⁸₆</td>
<td>-₶₀.₈₄₈₆</td>
<td></td>
</tr>
</tbody>
</table>
Table 28 Published reference values for the $^{117}\text{Sn}^\text{-1}H$ and $^{119}\text{Sn}^\text{-1}H$ coupling constants. More values obtained using different solvents are found in the publication of Petrosyan, Roberts and co-workers.\textsuperscript{a} In the same publication also the values for the related $^{119}\text{Sn}^\text{-13}C$ coupling constants are reported.\textsuperscript{a} The chemical shift was not reported, \textsuperscript{b} the solvent used for the measurement was not reported.

<table>
<thead>
<tr>
<th>Compound</th>
<th>156</th>
<th>157</th>
<th>158</th>
<th>137-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-C (Å)</td>
<td>1.8602(31)</td>
<td>1.847(2)</td>
<td>1.8668(5)</td>
<td>1.8522(19)</td>
</tr>
<tr>
<td></td>
<td>1.8646(42)</td>
<td>1.838(2)</td>
<td>1.8616(4)</td>
<td>1.8553(19)</td>
</tr>
<tr>
<td>Si-Me (Å)</td>
<td>1.8622(38)</td>
<td>1.865(2)</td>
<td>1.8694(5)</td>
<td>1.865(2)</td>
</tr>
<tr>
<td></td>
<td>1.8605(43)</td>
<td>1.860(3)</td>
<td>1.8705(4)</td>
<td>1.869(2)</td>
</tr>
<tr>
<td>α (°)</td>
<td>104.649(130)</td>
<td>101.16(10)</td>
<td>101.113(11)</td>
<td>104.02(8)</td>
</tr>
<tr>
<td>δ (°)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>121.68(15)</td>
</tr>
<tr>
<td>spiro α (°)</td>
<td>107.027(145)</td>
<td>127.24(17)</td>
<td>113.785(14)</td>
<td>118.61(15)</td>
</tr>
<tr>
<td>spiro δ (°)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>111.05(14)</td>
</tr>
<tr>
<td>9-azaanthracene fragment folding angle (°)</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>9-silaanthracene fragment folding angle (°)</td>
<td>32.131(170)</td>
<td>5.621(74)</td>
<td>47.852(8)</td>
<td>4.909(75)</td>
</tr>
</tbody>
</table>

Table 29 Structural comparison between the 9-silaanthracene fragment of compound 137-Si and the one of some selected examples.