SCUOLA DI SCIENZE
Dipartimento di Chimica Industriale “Toso Montanari”

Corso di Laurea Magistrale in

Chimica Industriale

Classe LM-71- Scienze e Tecnologie della Chimica Industriale

Synthesis and Characterization of fluorescent Atropoisomeric Bis-arylboryl-Carbazoles

Tesi di laurea sperimentale

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Anno Accademico 2020-2021

Abstract

This thesis project presents a work based on the study of bis-arylboryl-carbazoles a particular class of aminoboranes. The peculiarity of these compounds is the $^{-}B=N^{+}$ chemical moiety and their conformational behaviour coming from the combination of steric constrain and conjugation of the B-N bond. Our work is focused on three products: 9-(mesityl(naphthalen-1-yl)boraneyl)-9H-carbazole **1a**, 9-(mesityl(2-methylnaphthalen-1-yl)boraneyl)-9H-carbazole **1b** and 9-(anthracen-9-yl(mesityl)boraneyl)-9H-carbazole **1c**. We firstly focused our attention on the synthesis optimizing conditions. Then the products were synthetized and characterized with NMR. The products were eventually analysed through conformational studies, by a theoretical approach with DFT calculations and by experimental techniques, such as Standard kinetic and EXSY. In the end of this work the products were characterized through fluorescence studies both by DFT, TD-DFT calculations and experimentally by emission spectroscopy.

Sommario

Questo progetto di tesi si è basato sullo studio di bis-aril-boril-carbazoli. La peculiarità di questi composti è data dal sistema -B=N+ e dal loro comportamento conformazionale, dovuto alla combinazione di vincoli sterici e coniugativi del legame B-N. Il nostro lavoro si è focalizzato su tre prodotti: : 9-(mesitil(naftalen-1-il)boraneil)-9H-carbazolo **1a**, 9-(mesitil(2-metil-naftalen-1-il)boraneil)-9H-carbazolo **1b** and 9-(antracen-9-il(mesitil)boraneil)-9H-carbazolo **1c**. In primo luogo la nostra attenzione si è incentrata sulla sintesi ottimizzandone le condizioni. I prodotti sono stati sintetizzati e caratterizzati con l’uso della spettroscopia NMR. Sono stati poi svolti degli studi conformazionali dei prodotti sia attraverso approcci teorici con calcoli DFT sia con tecniche sperimentali, quali cinetica classica ed EXSY. Infine, i prodotti sono stati caratterizzati attraverso studi di fluorescenza sia tramite calcoli DFT, TD-DFT sia sperimentalmente con spettroscopia di emissione.

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Introduction

Aminoboranes

Functional materials are defined as any chemical system with useful physical or chemical properties. Materials that can convert external energy into direct molecular function are especially attractive. These stimuli responsive materials, also known as "smart" materials, are used for specialized applications.[1] Aminoboranes are materials that belong to this class and due to their luminescent properties have peculiar applications in OLEDs[2] and fluorescent sensors.[3] In the design of this material, incorporation of selected functional groups into π-conjugated carbon skeleton is a powerful strategy.[4] In this regard, the combination of the nitrogen filled p_z orbital with the boron empty p_z orbital generates a π-conjugated scaffold that enhances the chemical stability, also showing a small HOMO–LUMO gap. Thus, N-B bond-containing π-electron systems shows an unusual fluorescence.[4]

Twisted Intramolecular Charge Transfer State

The term fluorescence refers to the ability of some molecule to reemit radiatively with wavelengths higher than the absorption one. The fluorescence process can be rationalized in a process that involved three steps (Figure 1):

1. **Vertical absorption**: from the ground state (GS^{eq}), the molecule absorbs photons that raise it in the excited state ($ES^{no\text{-}eq}$).
2. **Non-radiative relaxation**: The unstable $ES^{no\text{-}eq}$ dissipates energy and reaches a minimum of energy in the excited state ES^{eq}.
3. **Vertical emission**: The molecule emits light and returns to an unstable ground state ($ES^{no\text{-}eq}$) that eventually reaches the ground state (GS^{eq}).

Theoretical studies have suggested that fluorescence in aminoboranes systems can be rationalized by considering the emission from the twisted intramolecular charge transfer state (TICT).[5]

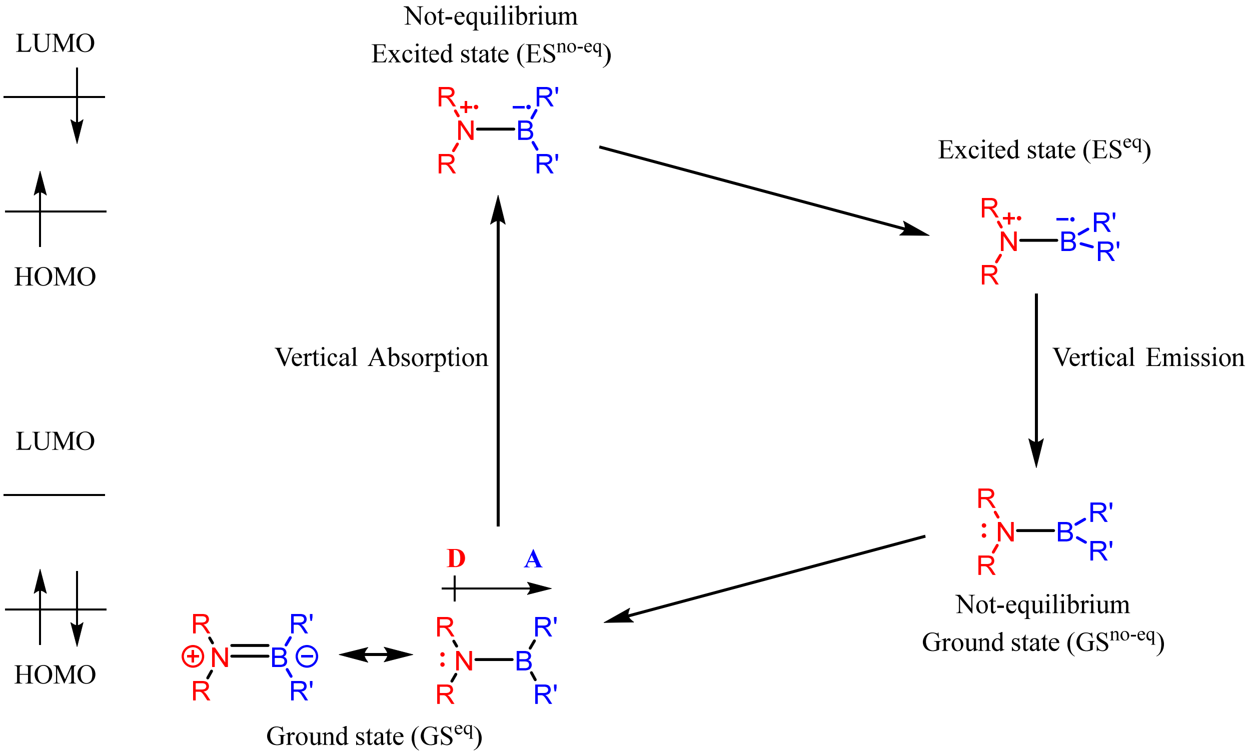


Figure 1. Representation of an emission process is shown for general aminoborane that involved TICT state.

In Figure 1, the TICT fluorescence process in the excited state of general aminoborane is represented. In the first step, thanks to the partial $^{-}B{=}N^{+}$ double bond, the molecule is almost planar. When the vertical absorption occurs, an electron in the HOMO is promoted in the LUMO, with anti-bonding character, leading to the destabilization of the system. In the second step, the molecule rearranges itself reaching a perpendicular conformation. This motion favours the charge transfer from nitrogen (Donating group, red) to boron (Acceptor group, blue) and improves stabilization by reducing the frontier orbital interaction. The character of charge transfer can be easily manipulated by adjusting several factors, including steric hindrance, polarity environments, effectiveness and strength of the Donor-Acceptor.[6] In the third step, from the ES^{eq} the molecule reemits light and reaches the $GS^{no\text{-}eq}$. According to Frank-Condon principles, atoms nuclei, during vertical emission or absorption, remain in the same position so the geometry is retained because vertical transitions are faster than molecular motions. At this point, the molecule can return in a planar conformation improving energy stabilization (GS^{eq}). The energy dissipation that occurs during the permanence of the molecule in the excited state makes that the wavelength of the emitted photons is greater than the wavelength of the absorbed photons. This difference is also known as “Stokes shift”. Not all the molecules that absorb energy can reemit with radiative processes. Collisions between molecules can quench fluorescence or even the molecule alone can vibrate dissipating energy. For this reason, the Quantum Yield (QY) of a luminescent compound is usually calculated. QY is defined as the ratio between the number of photons emitted and those absorbed. QY can assume values from 0 to 1 and it depends on the nature of the molecule and the environment (temperature, solvent, etc.).

Axial Chirality and Atropisomers

Stereochemistry of a molecule is related to the spatial arrangement of its atoms. Molecules with central chirality possess one or more stereogenic centres. The stereogenic centres are identified by a single atom bonded with four different substituents and for this reason they have no element of symmetry (mirror plane e/or centre of inversion). Thus, the spatial arrangement of the substituents on the atom leads to the existence of two enantiomers for each centre. The interconversion of these stereoisomers requires the breaking of a bond (Figure 2, right).

On the other hand, the axial chirality is characterized by stereogenic axes which are identified when the rotation around a single bond is restricted. This allows for the existence of two conformational isomers called atropisomers that are non-superimposable mirror images (*i.e.* two enantiomers). The stereoisomers identified by chiral axes can interconvert by rotation about single bonds. Biarylic systems are the most representative example of atropoisomeric compounds (Figure 2, left).

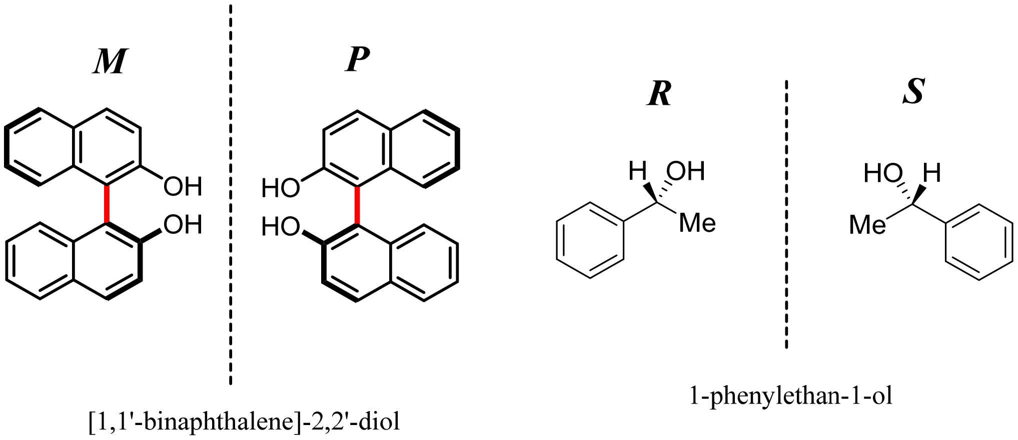


Figure 2 Left: atropisomers with chiral axis indicate in red, right: example of central chirality

The rotation around a bond is a time-dependent process and depends on several factors. The temperature, the steric hindrance and/or electronic interactions of the substituents close to the axis can slow down the rotation. An important requirement for the existence of chiral atropisomers is the presence of different substituents on the aryl rings on both sides of the chiral axis, to avoid the presence of a symmetry plane, responsible for non-chiral “*meso* forms” (Figure 3).

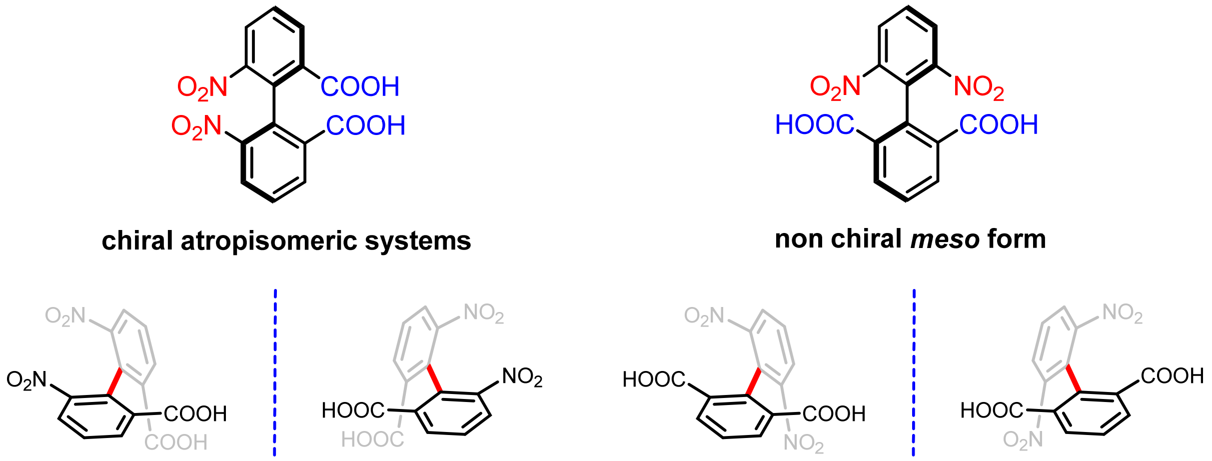


Figure 3. Left: chiral atropisomer; right: achiral meso form.

In 2011, LaPlante has proposed a useful evaluation of stereogenic axis stability.[7] According to this, conformational isomers can be classified in three different classes based on their rotational energy barriers (Figure 4).

- Class 3: In this class, conformational isomers have rotational energy barriers greater than 30 kcal/mol and consequentially half-lifetime of interconversion in order of years. Therefore, the single stereoisomer can be considered kinetically stable.
- Class 2: These molecules are in a metastable situation; rotational energy barriers are between 20 and 30 kcal/mol and half-lifetime of interconversion between minutes to years. Molecules with these features may not be physically resolved at room temperature (at 298 K). Therefore, it is possible to identify two subclasses:
    - Class 2a: Rotational energy barriers between 20 and 23 kcal/mol, the two possible stereoisomers can be detected and may be resolved, but rotation is fast enough at 298 K to complete racemization from minutes to hours.
    - Class 2b: 23 kcal/mol $< \Delta E_{rot} <$ 30 kcal/mol, enantiomerically pure atropoisomer can be detected, resolved, and stored at 298 K for hours to weeks.
- Class 1: The conformational isomers belonging to this class cannot be considered atropisomers at 298 K. Relatively fast axial rotation occurs in order from nanoseconds to a few seconds. The rotational energy barrier is generally less than 20 kcal/mol so it must be considered as single entities.

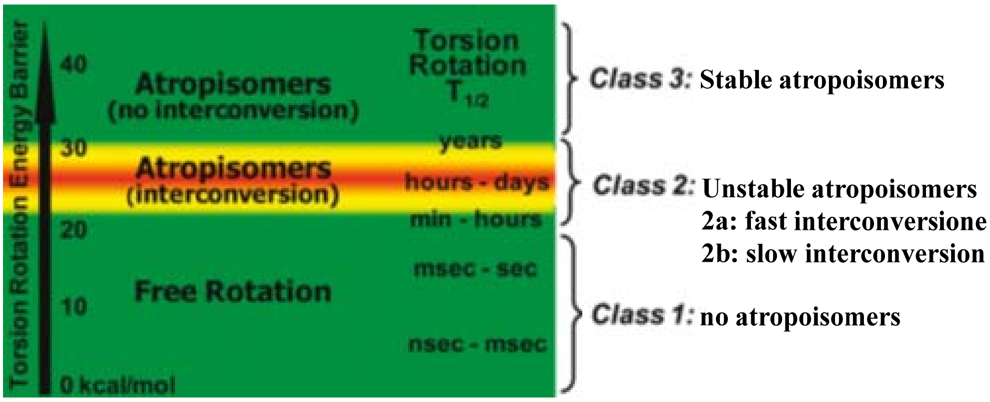


Figure 4 Rotational energy barrier at 298 K of the single atropoisomer. [reprinted and adapted from Laplante, S. R. et al. Assessing atropoisomer axial chirality in drug discovery and development. J. Med. Chem. **54**, 7005–7022 (2011)]

Stereochemical descriptors

The absolute configuration of two atropisomers that have a chiral axis is related to the dihedral angle between two planes. A dihedral angle is identified by four atoms called **a-b-c-d** (Figure 5). The first plane is identified by the atoms **a**, **b**, **c** and the other one by **b**, **c**, **d**. The torsion angle moving along the shortest path between the planes determines the absolute configuration. Atoms **b** and **c** are placed on the chiral axis while **a** and **d** are the substituent with highest priority (deduced with the CIP-rules) on the opposite side of the b-c bond. The absolute configuration is assigned *P* (Plus, positive dihedral angle) for clockwise torsion and *M* (minus, as negative dihedral angle) for counterclockwise torsion. *P* and *M* descriptors are also used to assign absolute configuration of helixes, in which *M* and *P* stands for the left- and right-handed helix respectively.

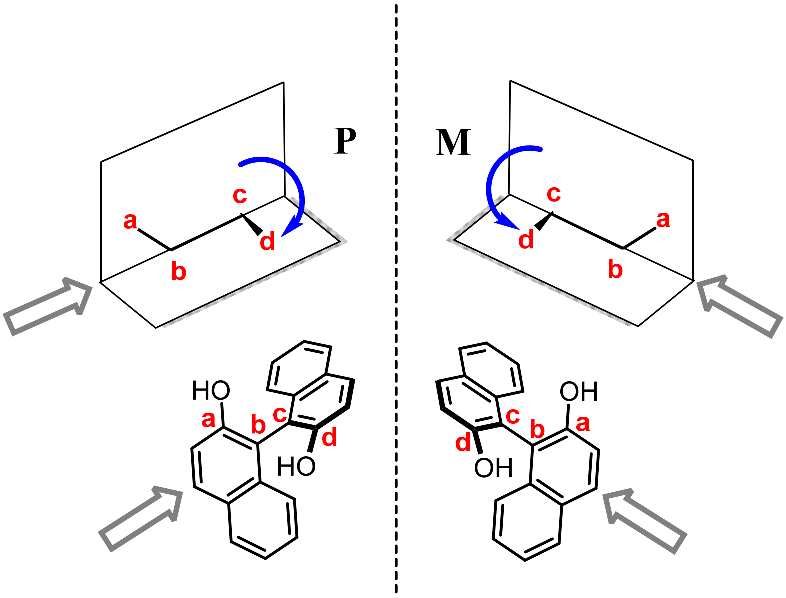


Figure 5 *P* and *M* descriptor representation for BINOL

N-borylcarbazole and *N*-borylbenzocarbazole

N-borylcarbazole and *N*-borylbenzocarbazole are compounds that are gaining increasing interest in literature due to luminescence proprieties (Figure 6).[8] The fluorescence character of these compounds is strongly dependent on the polarity of the solvent, making solvatochromic solutions. In these systems where the excited state shows TICT character, the solvent can stabilize or destabilize the excited state. During the electronic transition, the solvent molecules rearrange to respond to the change in the solute's dipole moment. The difference in the dipole moment between GS and ES affects their relative energies and influences all the representative parameters of fluorescence such as QY, Stokes shift and emission intensity. Hence, if the dipole moment of the GS is bigger than the ES, the solvent stabilizes much more GS and the emission shifts to shorter wavelengths (negative or blue shifts). On the contrary, when the solvent stabilizes ES, the emission shifts to longer wavelengths (positive or red shift).[9]

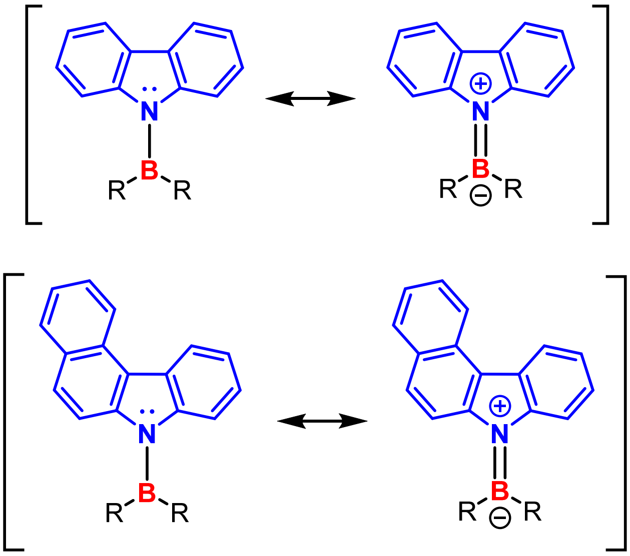
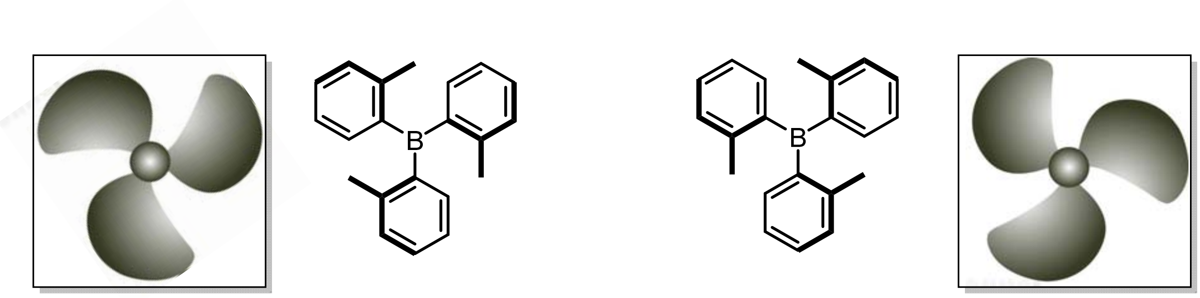


Figure 6 top: N-carbazoleborane, bottom: N-benzocarbazole borane

Due to the empty p_z orbital on boron, these kinds of systems usually have poor chemical stability towards nucleophilic attacks. To overcome this issue, aryl substituents with methyls in the *ortho* positions, such as mesityls, are usually bonded to the boron. These aryls can shield the boron atom by improving the chemical stability of these compounds, but also increasing the steric hindrance around the boron. For this reason, these systems have angled aryls giving propeller like conformations.

Molecular propellers

When two or more aryl rings (Ar) are linked to a single atomic centre (Z), the rotation of the Ar-Z bond axis is led by the other rings. Molecules of this type are propeller-like in shape. The aryl rings can be considered as “blades” with an axis of rotation, allowing the existence of chiral (helical) structures: right-handed (*P*) and left-handed (*M*) helix (Figure 7).[10] Trisarylboranes usually shows propeller-like conformations in the ground state, where the three blades are twisted out of the plane, considering the planar plane formed by the three carbons bonded to boron. The possible interconversion of stereoisomers occurs with “flip” mechanisms. The "flip" is considered the torsional movement of the rings around the boron atom. There are two possible flips: one in which a ring passes through the planar plane with a disrotatory movement and a simultaneous interchange of the sides; another in which the ring is perpendicular to the planar plane with a conrotatory motion and no exchange of the sides. Four possible mechanisms are reasonable: zero, one, two, or even three aryl ring systems can rotate together through the B-C bond axis (ring “flip”).[11] In the zero- and three-ring flips, all the ring move together in clockwise or counterclockwise respectively. With one- or two-ring flips, one ring rotates in the same direction while the remaining rings rotate in the opposite one.



left handed: *M*

right handed: *P*

Figure 7. Molecular propellers in tri-arylboranes

In this regard, Mancinelli and co-workers have reported the stereodynamic behaviour of bis-mesityl-boranes bearing carbazole or benzocarbazole.[8] According to the “ring flip” (RF) nomenclature proposed by Mislow,[11] the transition state geometries are identified regarding a reference plane where boron, nitrogen and two carbons of the mesityl groups atom linked to boron are contained. The prefix number identifies the number of rings that are perpendicular to the reference plane. The possible transition states are shown in Figure 8. Bis-mesityl-boranes develop a partial π-bond because the nitrogen filled p_z-orbital shares a pair of electrons with the empty boron p_z-orbital. The 3-RF and 1-RFs are too high in energy to be accessible while 0-RF could not be simulated due to the large steric hindrance of the geometry. Reasonably, the 0-RF cannot be accessible for the interconversion of conformers. The 2-RFs have two available geometries that have different stereochemical effects on the B-N branch of the molecule. When the two mesityl rings reach perpendicular position by a conrotatory motion, at the same time the carbazole will be positioned planar to the reference plane. In this geometry, the -B=N+ moiety develops the maximum stabilization due to the overlapping between the empty boron p_z orbital and the nitrogen lone pair. On the contrary, steric clash between the mesityl rings disfavours this geometry. This TS corresponds to the so-called steric barrier (Fig.8 2-RF left). When one mesityl ring and the carbazole are perpendicular to the reference plane, steric interactions between the mesityl rings decrease, but at the same time the B–N bond completely loses any π contribution. This TS corresponds to the conjugative barrier of the B–N bond (Fig.8 2-RF right).

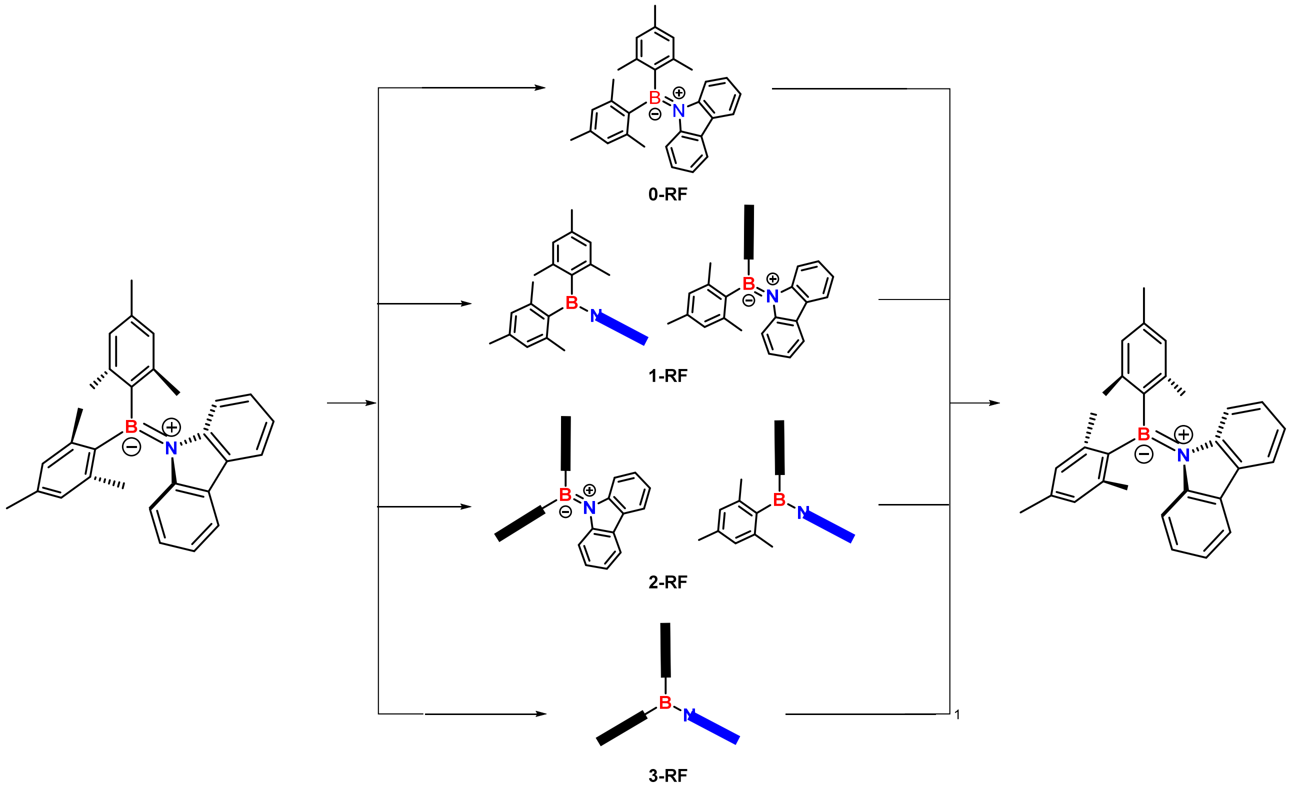


Figure 8. Graphic representation of the possible TSs is shown,

Kinetic studies

Strereodynamic processes can be experimentally evaluated by Dynamic-NMR and Dynamic-HPLC in a range of energies between 4.5 kcal/mol and 26 kcal/mol. However, in systems where rotational energy barriers exceed the values reported above, discontinuous technique can be used. Classic kinetic studies are performed isolating one enantiomer through chiral stationary phase (CSP) HPLC and racemized at high temperatures. In order to evaluate the evolution of racemization, small aliquots are collected at fixed times and injected at room temperature in CSP-HPLC.

The kinetic equation derived from a first order reversible process at equilibrium is:

$$ln(x_{eq} - x) = -2k_{rac}t + ln(x_{eq})$$

Eq. 1 kinetic equation

Where x is the molar fraction of the interconverted enantiomer in the corresponding time *t*; x_{eq} is the molar fraction of the same enantiomer reached at the equilibrium ($x_{eq} = 0.5$); k_{rac} is the rate constant (s^{-1}); t is time (s). The Eq. 1 represent a straight line in the form $y = mx + q$, where the slope is $-2k_{rac}$ and the intercept is $\ln(x_{eq} - x)$. The resulting k_{rac}value is eventually used to obtain the $\Delta G^{\neq}$ of the process (Eq. 1) from the derived Eyring equation (Eq. 2):[12]

$$k = \kappa \frac{k_B \cdot T}{h} e^{-\frac{\Delta G^{\neq}}{RT}}$$

Eq. 2 Eyring equation

Where h is the Planck's constant ($1.584 \cdot 10^{-34}$cal·s); k_B is the Boltzmann constant ($3.2998 \cdot 10^{-24}$); R is the universal gas constant (1.9872 cal/K·mol); κ is the transmission coefficient that can be considered equal to 1.

Solving for $\Delta G^{\neq}$ in kcal/mol (Eq. 3):

$$\Delta G^{\neq} = 4.574 \cdot 10^{-3} \cdot T \cdot \left(log \frac{T}{k} + 10.310 \right)$$

Eq. 3 kinetic equation solved for $\Delta G^{\neq}$

To evaluate experimental rotational energy barriers in a range between ~20 to ~22 kcal/mol the EXchange SpectroscopY (EXSY) experiment can be used. EXSY requires the irradiation of a single proton signal with the NOESY pulse sequences but with a mixing time in the scale of milliseconds. In this evolution time, the nearest protons do not develop NOE effect. During the mixing time, the proton irradiated can change its position in the space and interchange with another. The two protons interchanged exhibit EXSY signals in the NMR spectrum with a different ratio of integrals depending on the mixing time and temperature. The interpolation of the integrals and the mixing time by a kinetic first-order reversible at equilibrium will provide the rate constant and $\Delta G^{\neq}$.

Theoretical methods

Computational methods can be useful before the synthesis in the design of the molecules and to investigate steric requirements needed to obtain stable stereoisomers. In this regard, the

Density Functional Theory (DFT) is a computational methodology used to simulate the property of many-electron systems. The basic idea of DFT is that for a collection of electrons and nuclei the ground state molecular energy, the wave function and all other molecular electronic are uniquely determined by the electron density as a function of three spatial coordinates ρ(x,y,z). The ground state energy (E_0) is a function of ρ: $E_0 = E(\rho(\mathrm{r}))$.[13]
$E(\rho(\mathrm{r}))$ is derived from the linear combination of functional and one of them is not correctly known: the exchange-correlation functionals. Because of this uncertainty it is necessary to introduce approximations to the DFT method. Several functionals have been proposed to evaluate better the exchange-correlation functionals. B3LYP is the most used hybrid functional in organic chemistry. This functional linearly combines the Hartree-Fock exchange with the DFT exchange-correlation functionals, leading to integrals that can be solved with numerical methods. The functional defines the approximation of the exchange-correlation energy, while a combination basis set of functions describe mathematically each orbital of atoms.
Through DFT calculations is possible to obtain the conformations and energies of ground states but also find the geometries and energies of transition states. The accuracy of results from DFT calculations depends on the choice of the basis set and density functional. The calculate geometries and the relative energy of conformations, in many cases, can be experimentally checked with X-ray diffraction and kinetic studies respectively. The simulation of transition state structure and energy is a crucial point for dynamic analysis as a correct simulation can help to understand the process and to identify the correct experimental method to observe it.
In order to simulate fluorescence cycle, all the geometries and energies of the species involved need to be calculated. The optimization of GSs geometries is calculated with the DFT method describe above, while the optimization of excited state and the vertical transitions are calculated with TD-DFT method because the light-matter interaction processes, like fluorescence, are time dependent (TD).[15] Therefore, Time Dependent-Density Functional Theory (TD-DFT) is employed and CAM-B3LYP is used as functional. Fluorescence processes are affected by the polarity of the solvent. This leads to define a computational model integrated in DFT and TD-DFT methods for simulating contributions of solvation. The PCM (polarizable Continuum Model) with SCRF (Self-Consistent Reaction Field) method can determine the wave function that describes the solute-solvent interaction.[9]

Electronic Circular Dichroism

Electronic Circular Dichroism (ECD) analysis can observe the different ability of chiral molecules to absorb left or right circularly polarized radiation at wavelength compatible with electronic excitation (UV-VIS spectra). The Electronic Circular Dichroism (ECD) signal for a chiral substance is the difference between the absorbance of left and right circular polarized light. The CD signal is expressed in the difference of the molar attenuation coefficient because it is independent by the concentrations *c* and the path length *l*.

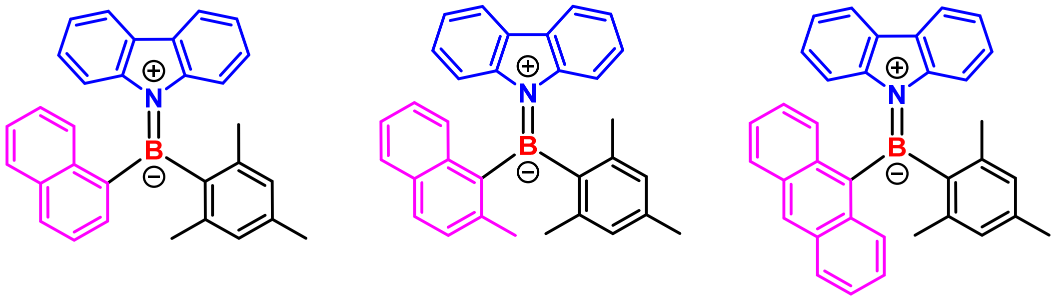
$$\Delta\varepsilon = \varepsilon L - \varepsilon R = CD/cl$$

Usually, the ECD spectra are represented as the variation of $\Delta\varepsilon$ in function of the wavelength. Racemic and achiral substance have a flat ECD spectrum because the sum of the absorption left and right circularly polarized light (L-CPL and R-CPL) results zero.

The ECD signal depends on the nature and disposition of the chromophores in the molecular structure. In this regard, the electronic environment of each chromophore gives important information about the conformation. Moreover, the ECD spectrum is useful to the determination of absolute configuration giving opposite spectrum for a pair of enantiomers. The absolute configuration is determined by comparison between the experimental ECD spectrum to the calculated one using TD-DFT method.

Aim of the thesis

The work of the thesis was focused on the synthesis of bis-arylboryl-carbazole **1a**, **1b**, **1c** (Figure 9). A new synthesis and its optimization were done, starting with a synthesis reported by Mancinelli in 2021.[8]



1a **1b** **1c**

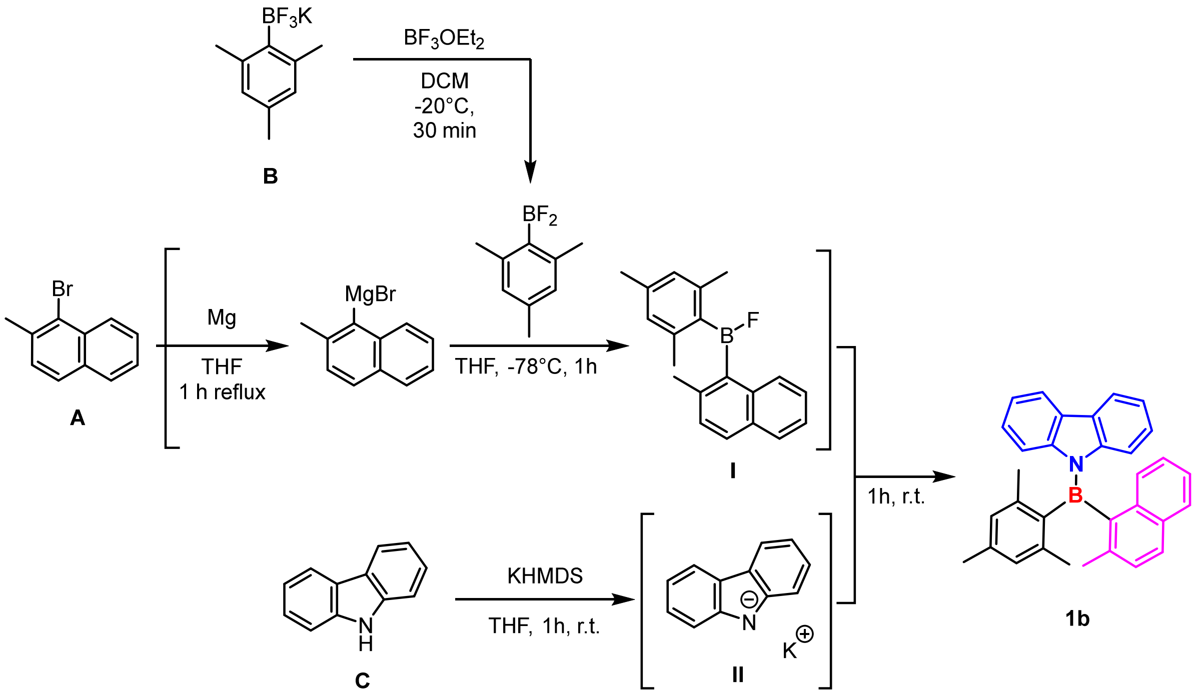
Figure 9 Products **1a**, **1b**, **1c**

The rotational barriers of the synthetized products were measured with standard kinetic and 1D-EXSY-NMR techniques. Additional attention was paid for the luminescent properties of the products. The absorption wavelength, emission wavelength and the Stokes Shift of all the products were calculated in three different solvent with increasing polarity: *n*-hexane (HEX), tetrahydrofuran (THF), acetonitrile (ACN) by DFT, TD-DFT level theory. The products were characterized by emission spectra were registered in collaboration with Stagni's research group.

Results and Discussion

Synthesis bis-arylboryl-carbazoles 1a, 1b, 1c

In the previous work, research group reported the synthesis of unsymmetrical substituted bis-arylboryl-carbazoles (Scheme 1).[15] Potassium mesityl-trifluorborate was used as boron source and was readily available by the reaction with KHF_2 of the corresponding mesityl-boronic acid. To avoid hydrolysis of the aryl-trifluorborates or any other fluoro-boron intermediates,[16] all the steps of the synthesis were performed under Argon atmosphere. Reagent **A** was chosen as starting material for the study of the reaction to give compound **1b**.



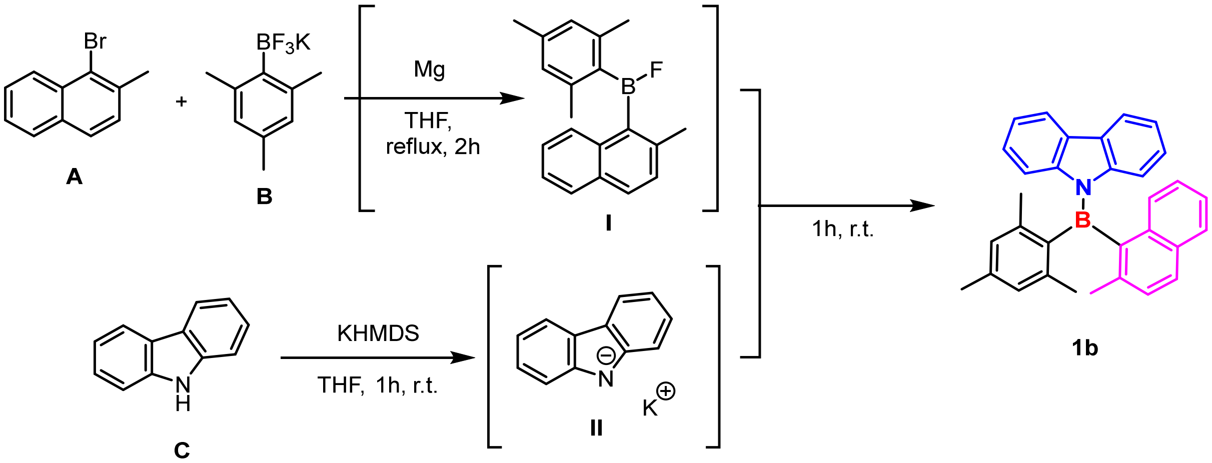
Scheme 1 General synthesis

In Scheme 1, the synthetic route was represented and it consists of three steps. In the first step, 1-bromo-2-methylnaphthalene (**B**), an excess of magnesium foils and a catalytic amount of iodine were kept at reflux in THF. The mixture was stirred and left to reflux for 2 hours after the discoloration of red iodine solution, obtaining the Grignard reagent.

In another flask, mesityldifluoroborate was prepared from potassium mesityltrifluoroborate and boron trifluoride diethyl etherate (BF_3OEt_2).

In the second step, the temperature of the Grignard reagent solution was decreased at -78 °C and the solution of mesytildifluoroborate was added dropwise to afford the intermediate **I**. In the third step, freshly prepared carbazole anion (**II** or **I)** was added and reacted for one hour. Following this procedure, the final product **1b** was obtained with 20% of yield over three steps. In order to avoid the use of corrosive BF_3OEt_2 and to reduce the reaction steps, the activation of potassium mesityltrifluoroborate was investigated.

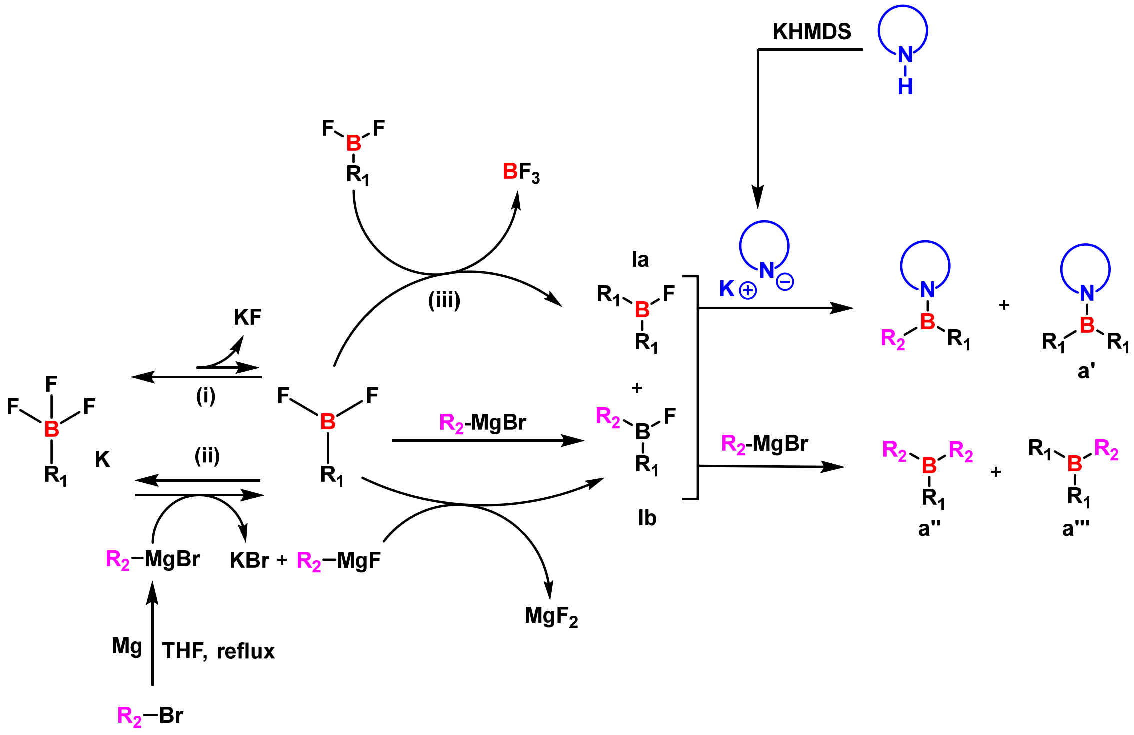
Ligand exchange from potassium ariltrifluoroborates salts of KF to form the active aryldifluoroborate intermediate can be mediated by fluorophores. Many fluorophores have been studied in literature, such has BF_3 or Si-based compound like TMSCl.[17] The conversion arytrifluorobarates species into aryldifluoroborate could be supplied by fluorophores such as Mg^{2+} or Li^+ cations, as reported in literature.[18] In this way, it was possible to try a one-pot reaction by activating the mesityltrifluoroborate with a Grignard reagent prepared *in situ* and reported in Scheme 2.



Scheme 2. Path a: “one pot” synthetic procedure

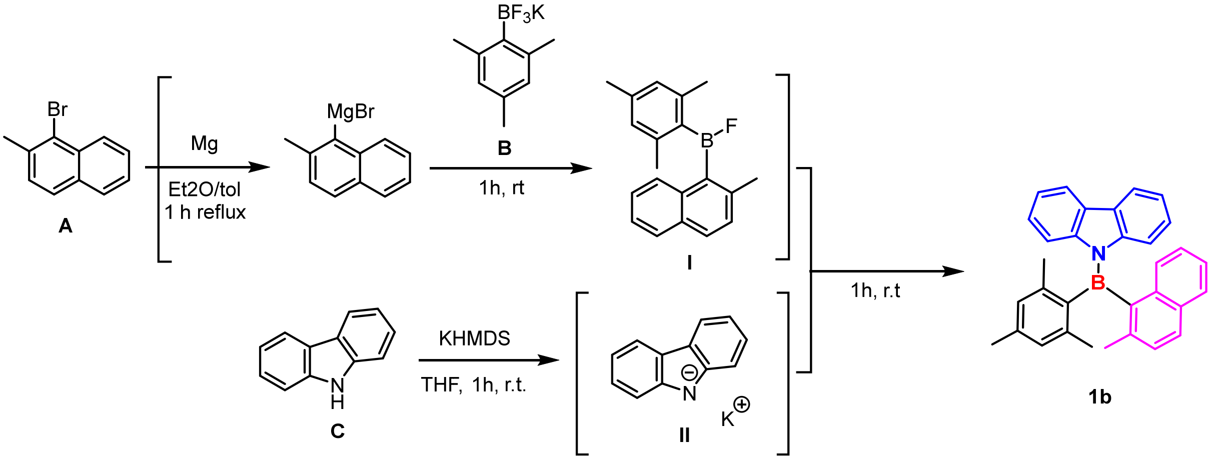
The one pot procedure was done adding together the aryl-bromine and the mesitylfluoroborate then refluxing for two hours. The temperature solution was decreased to room temperature and the carbazole anion was added. The solution was stirred for 1 hour providing the final product **1b** with 23% yield over two steps. To optimize the last step conditions, three bases for the deprotonating of carbazole were tested. NaH, *t*-BuLi and KHMDS were tested, but no significant differences were found in the yields. Therefore, the nature of the counterion has not appreciable influence reaction between **I** and **II**. Deprotonation of carbazole **C** was carried out with KHMDS for his facile handling.

The formation of **I** was checked with ^{19}F NMR experiment. The ^{19}F NMR spectrum showed different fluorinated by-products (Figure 10). As reported by Chambers and Chivers, aryldifluoroborate can be slow converted *via* dismutation at room temperature [19] and it is accelerated by heating. Therefore, in Scheme 3 it is represented the assumed mechanism of the reaction and the corresponding by-product (**a’**, **a’’**, **a’’’**) that could be formed. The high temperature required to prepare the Grignard reagent leads to dismutation (**iii**) of mesityl difluoroborate into bis-mesityl fluoroborate. This results in the existence of two reactive intermediates in the first step of reaction (**Ia** and **Ib**). Furthermore, **Ia** and **Ib** intermediates can also react with another molecule of Grignard to yield **a’’** and **a’’’**. When carbazole anion is added, a mixture of the desired product and **a’** is generated. Despite all proposed by-products only **a’** and **a’’** compounds has been detected by 1H-NMR.



Scheme 3 Proposed mechanism of the synthesis

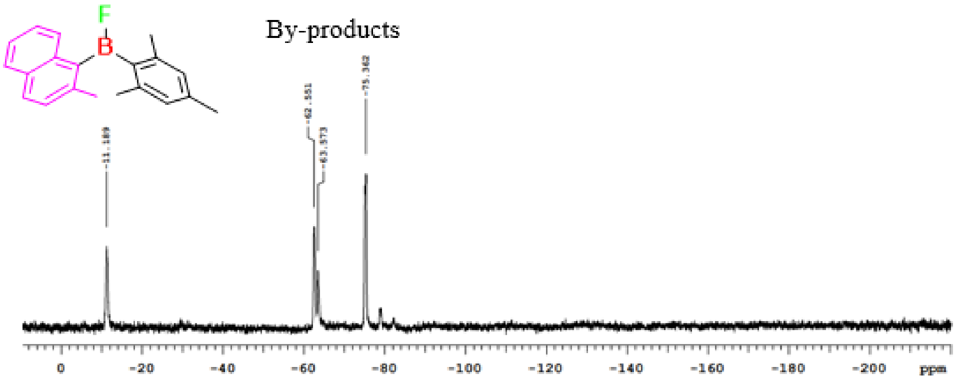
In this context, to avoid by-products and increase the yield, the Grignard reagent was added to dry THF solution of potassium mesityl-trifluoroborate salt. The temperature of the addition was tested at -10 °C and -78 °C, in order to reduce the energy for the disproportion but only a small amount of intermediate **I** was formed raising a poor yield of the final product. A recently new approach reported the preparation of unsymmetrically substituted tri-arylborane,[20] where the potassium mesityl-trifluoroborate was added on fresh prepare Grignard reagent at room temperature improving good yields. Thanks to this, a new synthetic strategy was proposed (***path b***, Scheme 4).



Scheme 4. Path b

Some difference was applied to the new procedure; THF were replaced by Et_2O/toluene as solvent to prepare the fresh Grignard intermediate; potassium mesityl-trifluoroborate were directly added to a room temperature Grignard solution. The formation of **I** was checked at ^{19}F NMR following *path b* (Figure 10).

Path a



Path b

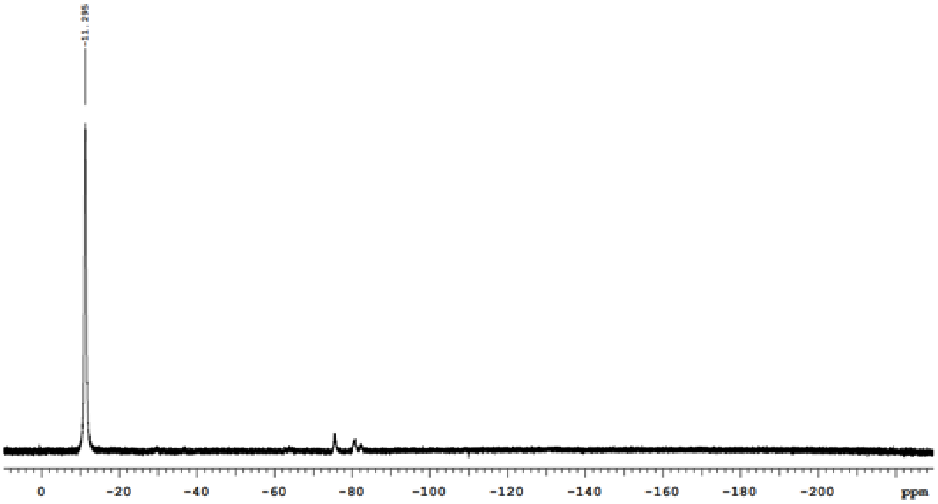


Figure 10 ^{19}F-NMR spectra of Mes-2methylnaphthylfluoroborate

NMR spectra revealed that following *path b* only a few by-products were formed. In comparison with *path a, the new reaction results very clean*. In fact, *path b* afforded the major yield of product **1b** (83%). After the optimization of the synthesis, product **1a** and **1c** were obtained with 43% and 32% yield respectively.

Conformational analysis

As discussed in the *molecular propellers* chapter, bis-arylboryl-carbazoles have a propeller-like structure. The presence of a different aromatic ring in the place of a mesityl does not change the idea of propeller flip but increase the number of possible 2-RF transition states. In addition to Mislow's RF nomenclature, three descriptors were added. Specifically, two letters that indicate which rings are perpendicular to the planar plane (i.e. **CC** for aryl-aryl and **CN** for aryl

-carbazole), then the shorted name of the planar ring (i.e. **carb** for carbazole, **ant** for anthracene and **mes** for mesityle).

When the aromatic ring is an anthracene (compound **1c**), the possible 2-RF transition states are three. The steric barrier has the carbazole planar and two aryl rings perpendiculars (2RF-CC-carb). While conjugative barrier has two different TSs depending on which mesityl (2RF-CN-mes) or anthracene (2RF-CN-ant) is planar, meanwhile the carbazole along with the other aromatic ring are perpendicular to it (Figure 11). All the transition states lead to an inversion of the helix and therefore lead to the exchange of two conformational enantiomers.

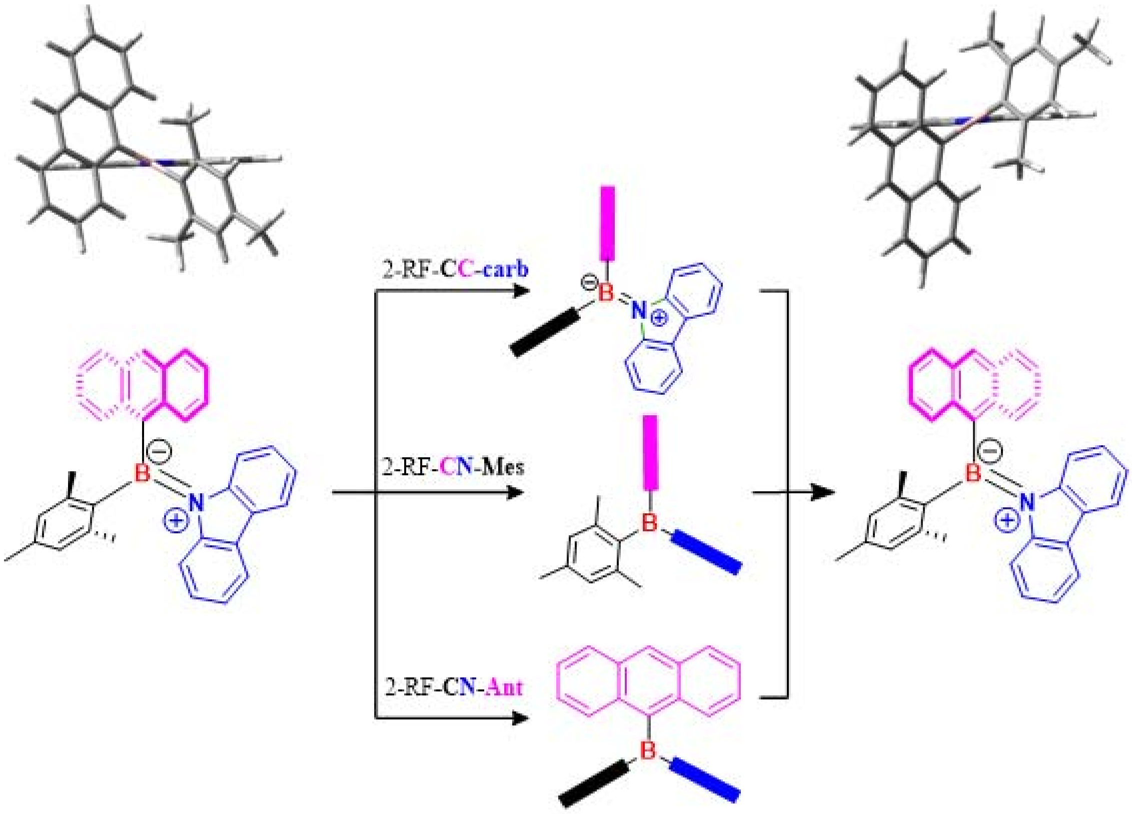


Figure 11 transition state of the compound **1c**

The compound **1a** and **1b** generate a more complex dynamic stereochemistry. Asymmetric naphthyl and 2-methyl-naphthyl rings add a chiral axis, increasing the number of transition states and ground states. In the ground states, two conformers for each enantiomer (i.e. *P*-GS1 and *P*-GS2) are possible coming from the inversion of the helix while the chirality of the axis is retained. There are two possible TSs to interconvert these conformers: 2RF-CC-carb and 2RF-CN-Mes (compound **1a** in Figure 12 and compound **1b** in Figure 13).

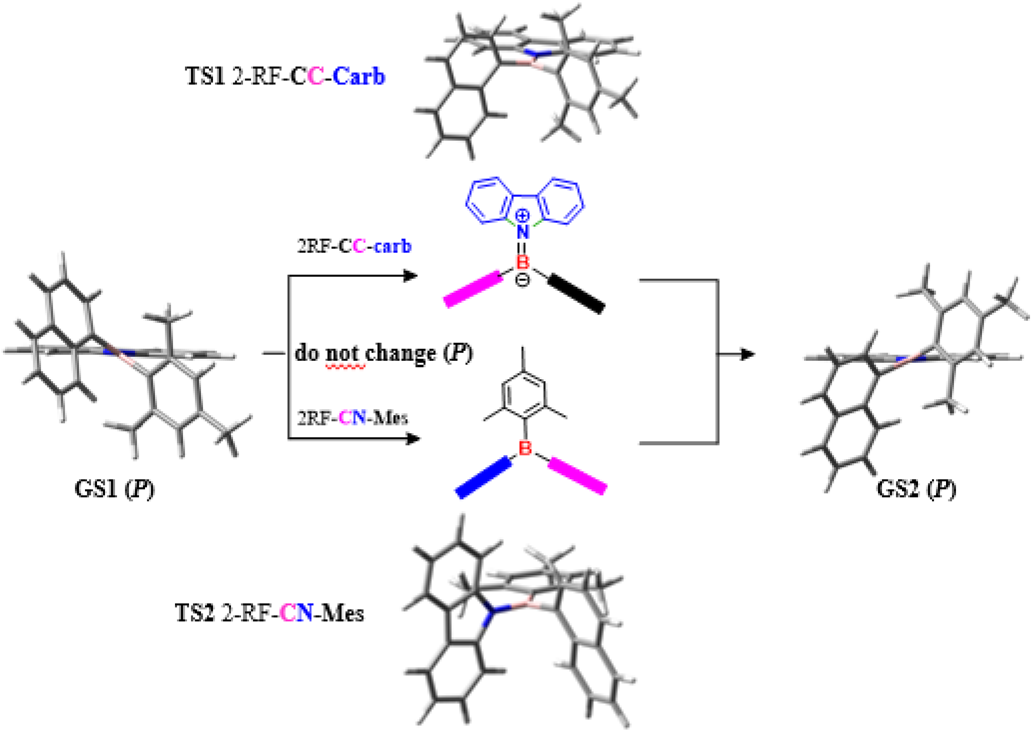


Figure 12 TSs of compound **1a** without changing chirality

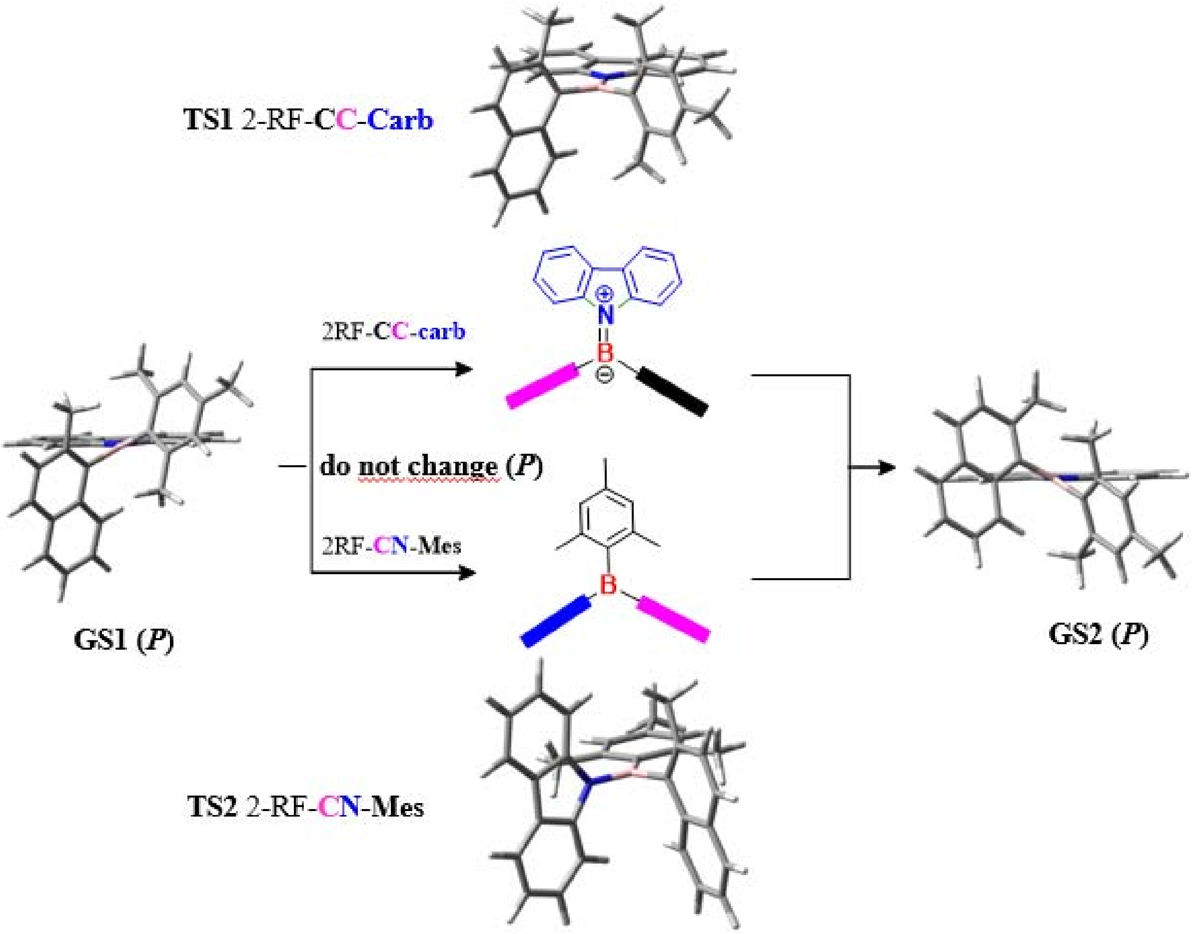


Figure 13 TSs of compound **1b** without changing chirality

Transition states with asymmetric ring in planar position implies the inversion of the chiral axis from *P* to *M* atropisomers. There are two possible transition states where the aromatic ring can rotate from the side of carbazole (2-rf-CN-Np0) or from the side of mesityl (2-rf-CN-Np180).

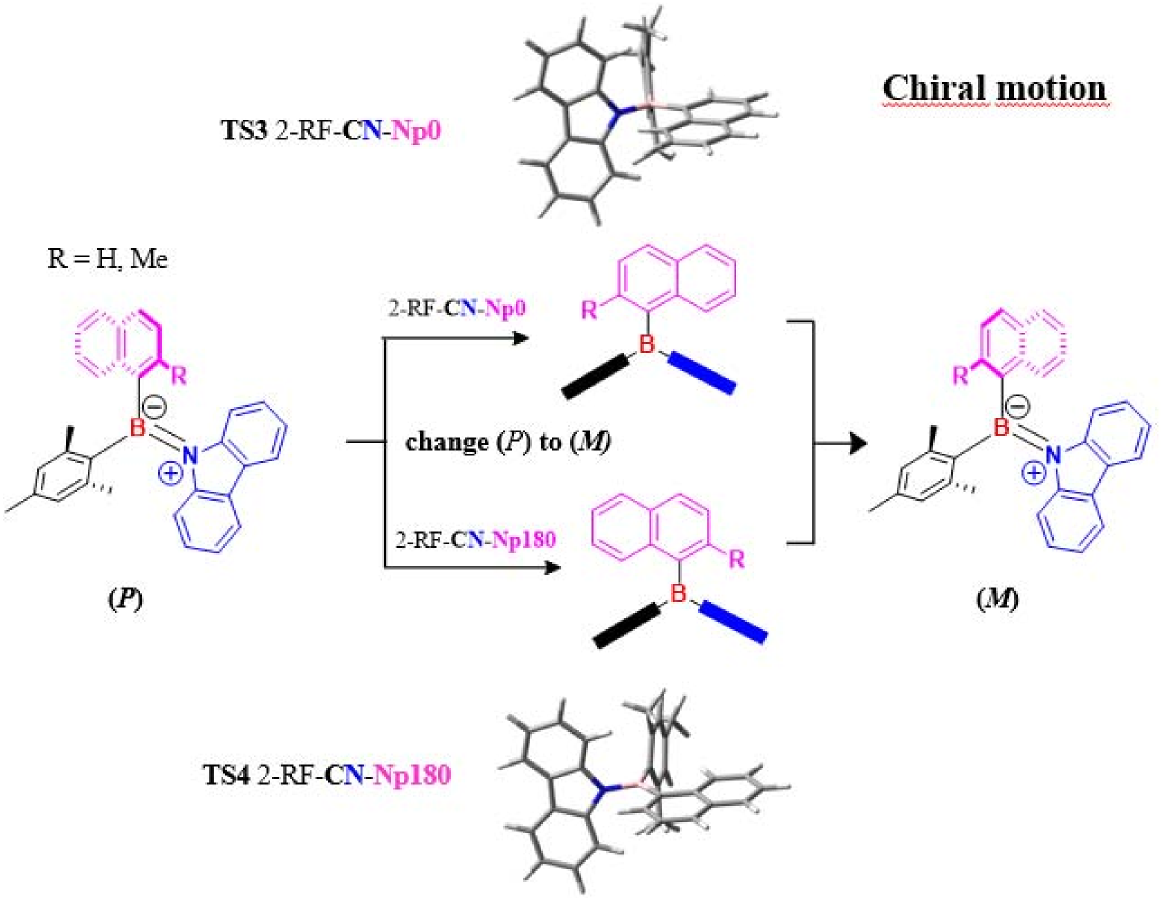


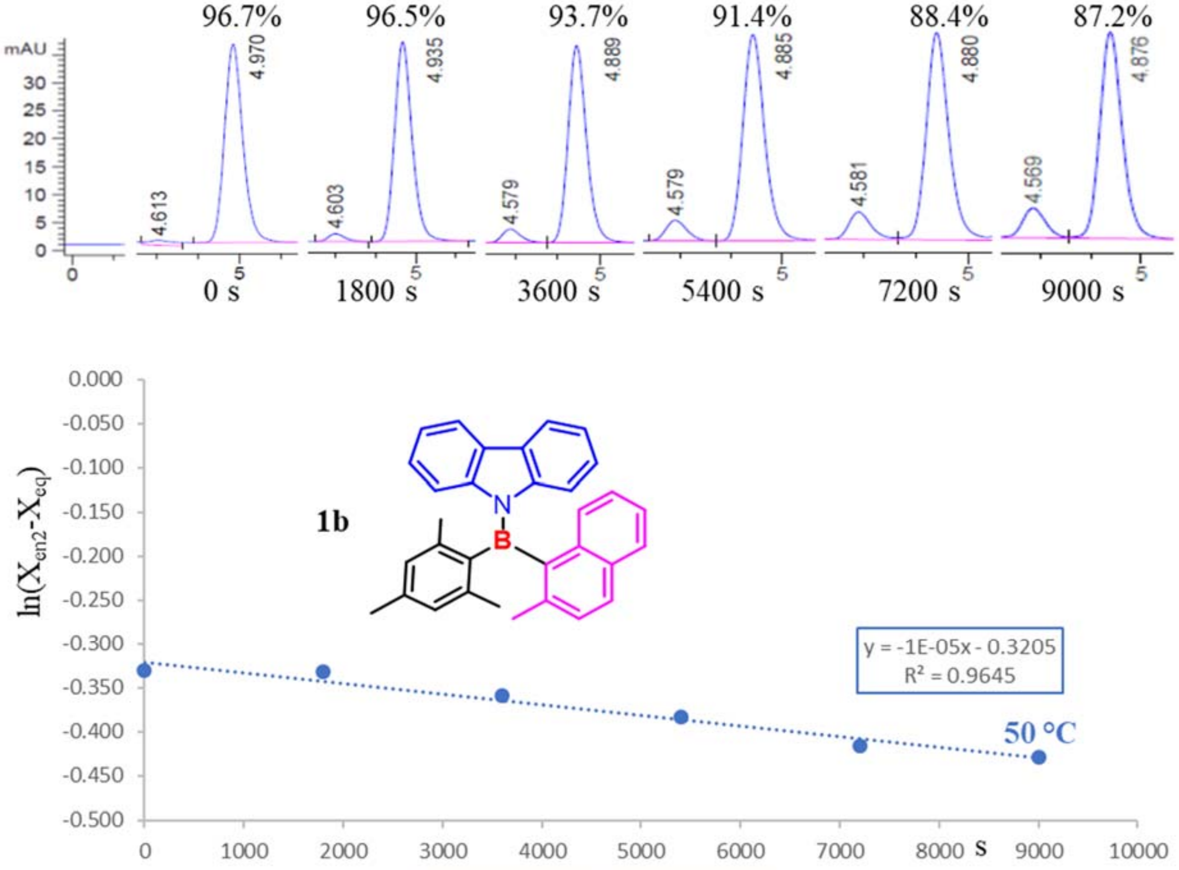
Figure 14 schematic representation of transition states with chiral motion is shown

In order to identify the energies of the two-ring flip motions and mostly the stability of atropoisomeric scaffolds, all the GSs and the TSs of the products were calculated with DFT level of theory and data are reported in Table 1.

Table 1. Relative energy barriers for two-ring flip motions (energies in kcal/mol) are reported.

Comp	**GS1**	**GS2**	**2RF-CC-carb**	**2RF-CN-mes**		**2RF-CN-Ar0** **2RF-CN-Ar180**	
			Calc.	Calc.	Exp.	Calc.	Exp.
1a	1.1	0.0	7.6	21.6	-	20.7 19.9	**20.9**
1b	0.4	0.0	11.4	23.5	**24.6**	26.4 25.3	**26.7**
1c	0.0	-	9.7	22.5	**23.9**	25.6 -	-

Compound **1b**, which has the more hindered 2-methylnaphhtyl, has a calculated energy barrier of 25.3 kcal /mol, high enough to resolve two atropisomers by CSP-HPLC. The racemization barrier of 26.7 kcal/mol was obtained by classic kinetic analysis (Figure 15). The free energy barrier corresponds to the TS4-2rf-CN-Ar180.



tempo (s)	T (°C)
	50
	ln(Xen2-Xeq)
0	-0.331
1800	-0.332
3600	-0.359
5400	-0.383
7200	-0.416
9000	-0.429
ΔG≠ (kcal/mol)	26.7

Figure 15 Kinetic analysis starting from the second eluted atropoisomer of compound **1b**.

In order to evaluate conjugative barriers of compound **1a**, **1b** and **1c**, EXSY analysis is performed. Therefore, we decided to irradiate one signal proton of carbazole with different mixing times. With the increasing of the mixing time, the molecule has more time to rotate in the NMR time scale and so, the signal of the other corresponding proton (8H) will be irradiate itself and generating an EXSY NMR signal. To understand better the process, in Figure 16 there is the schematization of the movements.

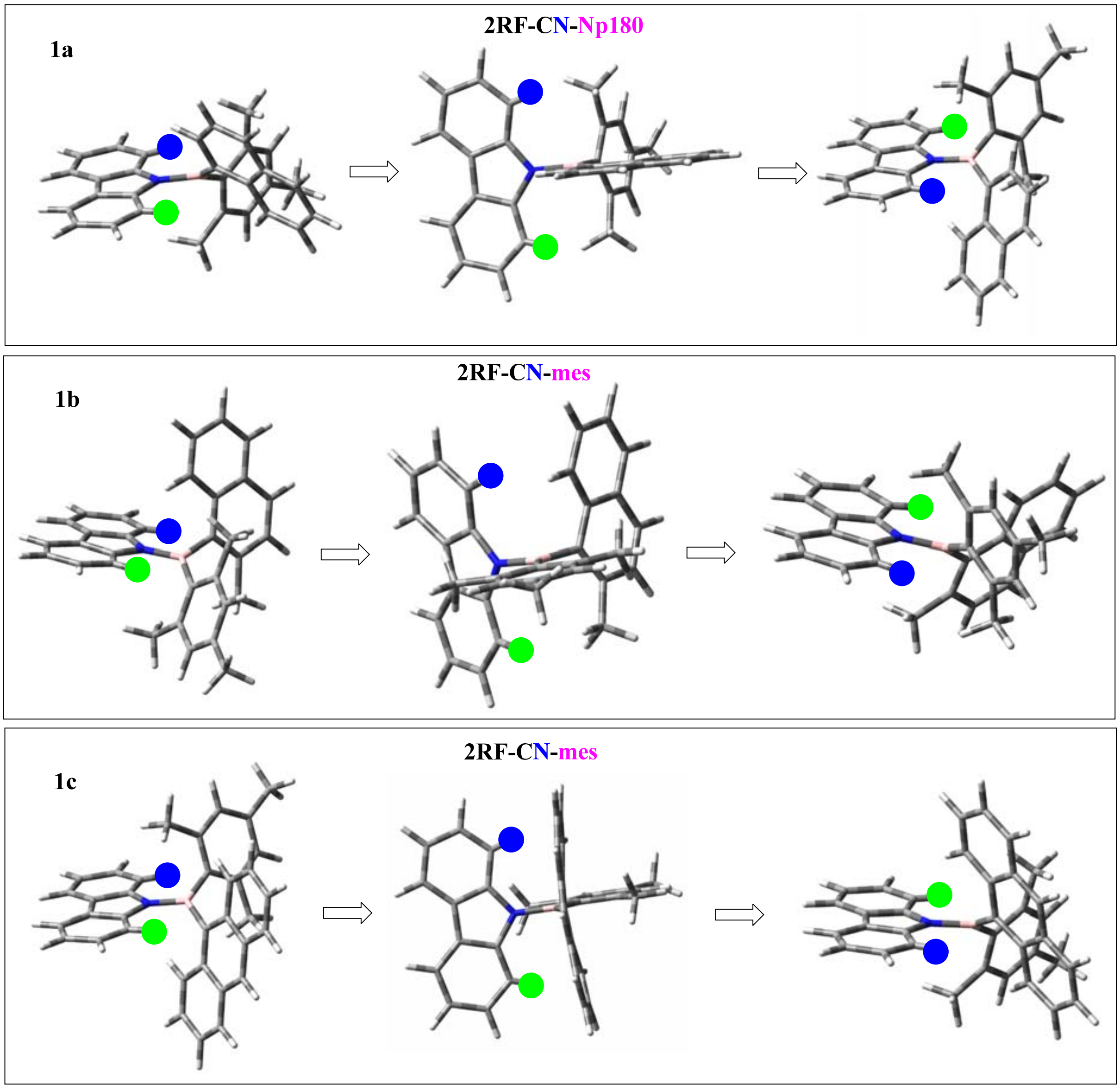


Figure 16 1H and 8H exchange of the carbazole in all the product structures.

The proton of carbazole is irradiated with six different mixing times at different temperatures. It is important to evaluate the results of more than one temperature to get a more accurate $\Delta G^{\neq}$. Transition states that involved rotation of carbazole is slow at room temperature. Hence, analysis requires higher temperatures that allows fast rotation of carbazole. This kind of analysis can unequivocally give the energy referred to the rotation of the carbazole, since the other motion of the molecule would not show any visible effect on the irradiated proton.

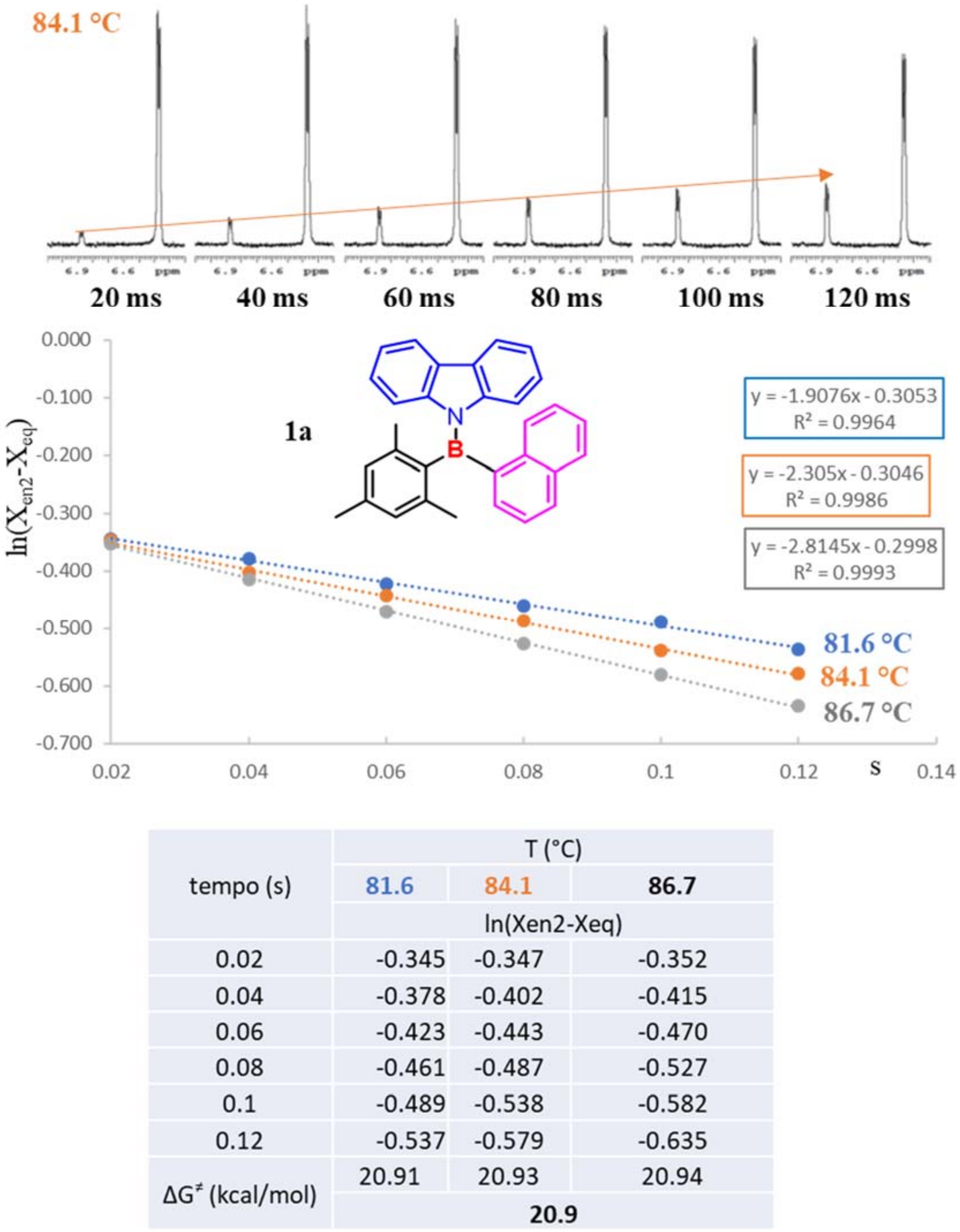
The EXSY experiment is considered a kinetic of the first order reversible to equilibrium. At 0 ms, the 100% of the signal is the irradiated proton, while for an infinite time it is reached an equilibrium (50:50) between the irradiated proton and the exchanged one.

The equation for a first-order reversible reaction is such as Eq. *1*:

$$\ln\left(X_{irr} - X_{irr\,eq}\right) = -2k \cdot t_{mix} + \ln(X_{irr\,0} - X_{irr\,eq})$$

Where X_{irr} is the percentage of the irradiated signal, $X_{irr\,eq}$ corresponds to the equilibrium (which is 0.5), $X_{irr\,0}$ is the percentage at zero time (which is equal to 1), t_{mix} is the mixing time and k is the rate constant.

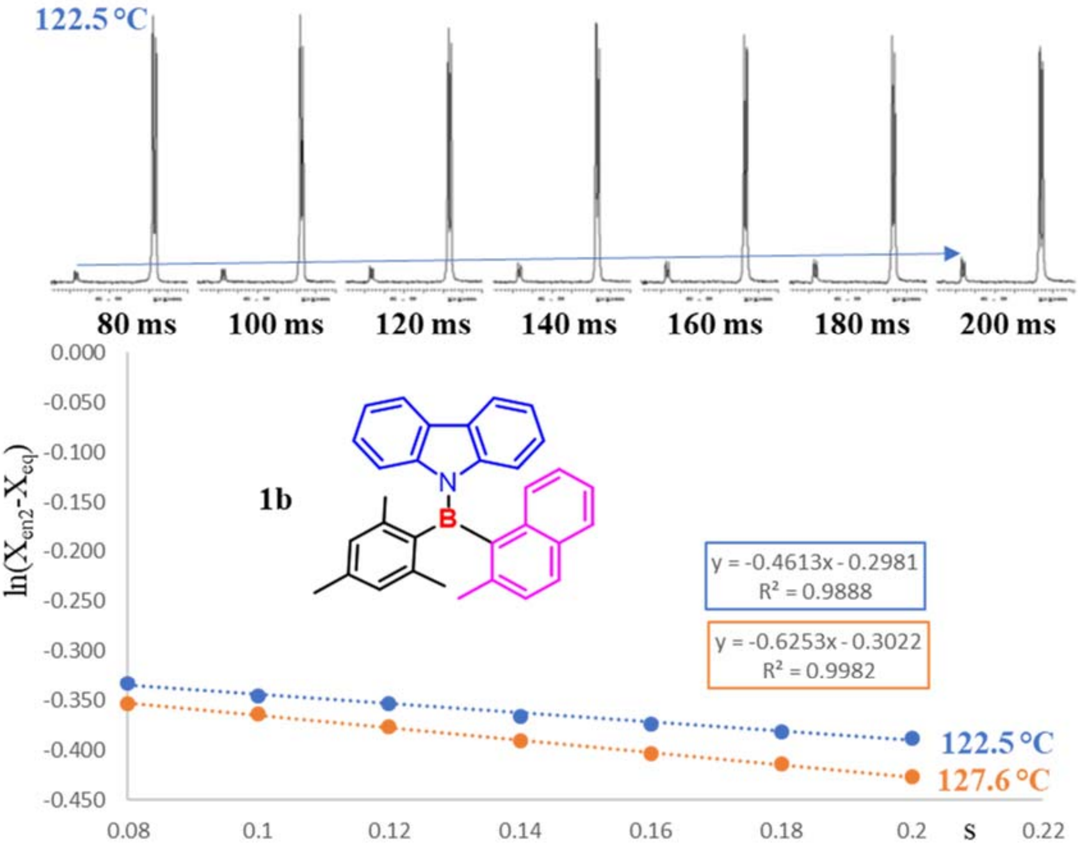
For compound **1a**, the EXSY analysis was conducted at three temperatures (+81.6 °C, +84.1 °C, +86.7 °C). After interpolation (Figure 17), we obtained a value of 20.9 kcal/mol which is consistent with the DFT calculated results. The free energy barrier corresponds to the lower 2RF-CN transition state and in this case it is 2RF-CN-Ar180 (see table 1).



tempo (s)	T (°C)		
	81.6	84.1	86.7
	ln(Xen2-Xeq)		
0.02	-0.345	-0.347	-0.352
0.04	-0.378	-0.402	-0.415
0.06	-0.423	-0.443	-0.470
0.08	-0.461	-0.487	-0.527
0.1	-0.489	-0.538	-0.582
0.12	-0.537	-0.579	-0.635
ΔG≠ (kcal/mol)	20.91	20.93	20.94
	20.9		

Figure 17 1D-EXSY spectra were acquired at three different temperatures (+81.6, +84.1 and +81.7 °C). Three rate constants are derived and an average energy barrier of compound **1a** was determined.

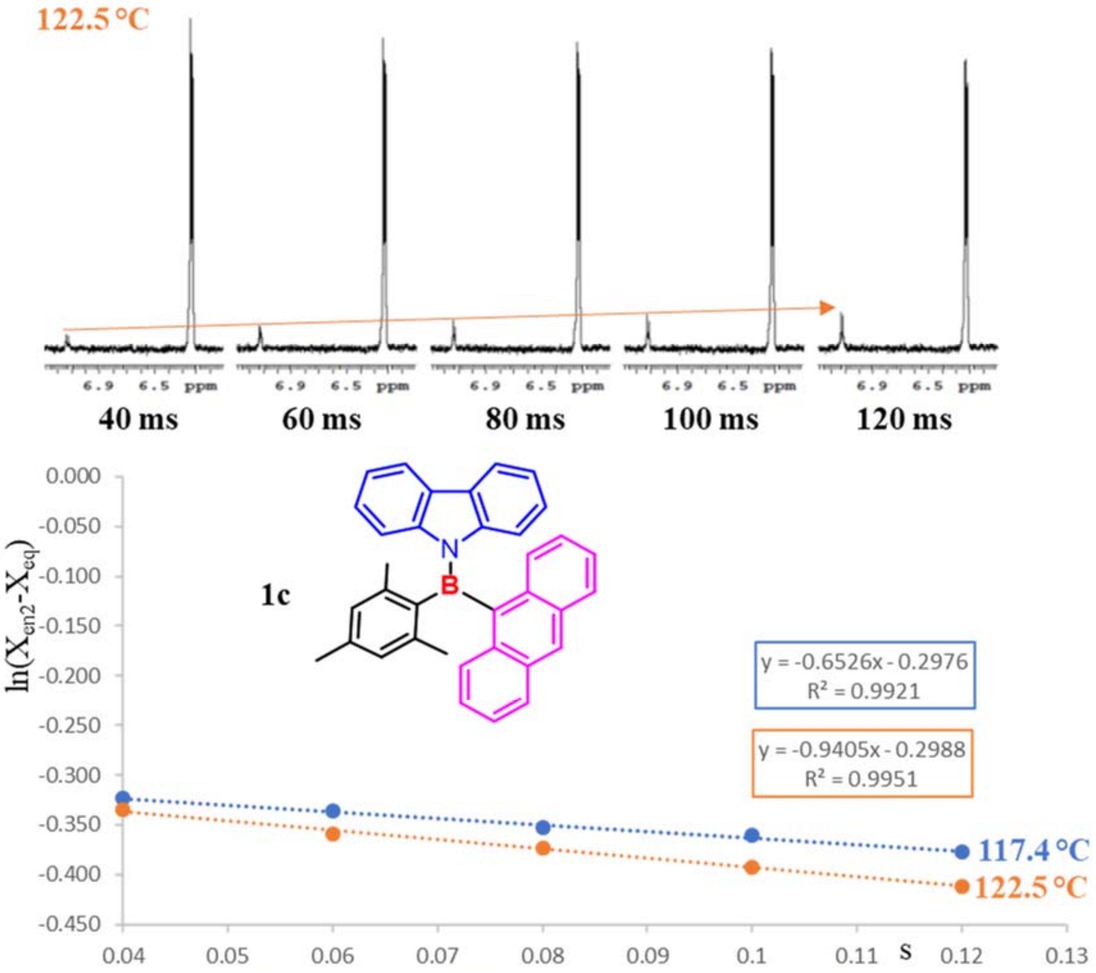
EXSY analysis was conducted for Compound **1b** at 122.5 °C and 127.6 °C and the free energy barrier corresponds to the **TS2-2rf-CN-mes** was 24.6 kcal/mol (Figure 18).

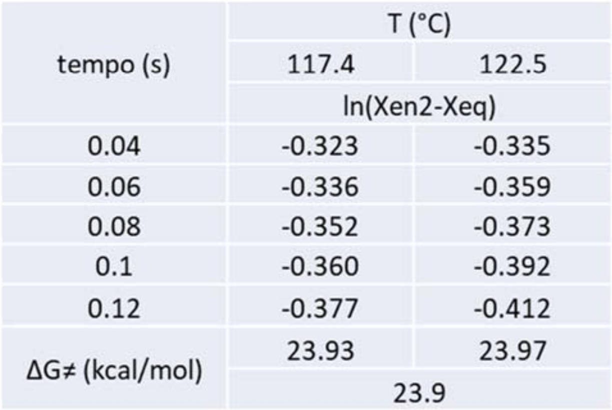


tempo (s)	T (°C)	
	122.5	127.6
	$\ln(X_{en2}\text{-}X_{eq})$	
0.08	-0.332	-0.353
0.1	-0.345	-0.363
0.12	-0.353	-0.377
0.14	-0.366	-0.391
0.16	-0.374	-0.404
0.18	-0.381	-0.414
0.20	-0.388	-0.427
ΔG≠ (kcal/mol)	24.52	24.61
	24.6	

Figure 18 1D-EXSY spectra were acquired at two different temperatures (+122.5 and +127.6 °C). Two rate constants are derived and an average energy barrier of compound **1b** was determined.

Rotational barrier for compound **1c** was **23.9** kcal/mol and it is consistent with DFT calculations for corresponding **TS2-2rf-CN-mes** (Figure 19).





tempo (s)	T (°C)	
	117.4	122.5
	ln(Xen2-Xeq)	
0.04	-0.323	-0.335
0.06	-0.336	-0.359
0.08	-0.352	-0.373
0.1	-0.360	-0.392
0.12	-0.377	-0.412
ΔG≠ (kcal/mol)	23.93	23.97
	23.9	

Figure 19 1D-EXSY spectra were acquired at two different temperatures (+117.4 and +122.5 °C). Two rate constants are derived and an average energy barrier of compound **1c** was determined.

The theoretical calculation of ECD spectra was selected to assign the atropoisomeric *P*/*M* configurations of compound **1b**. In order to compare the calculated spectra to the experimental one, the weighting sum of both GS1 (32.6%) and GS2 (67.4%) spectra must be considered (Figures 19 and 20).

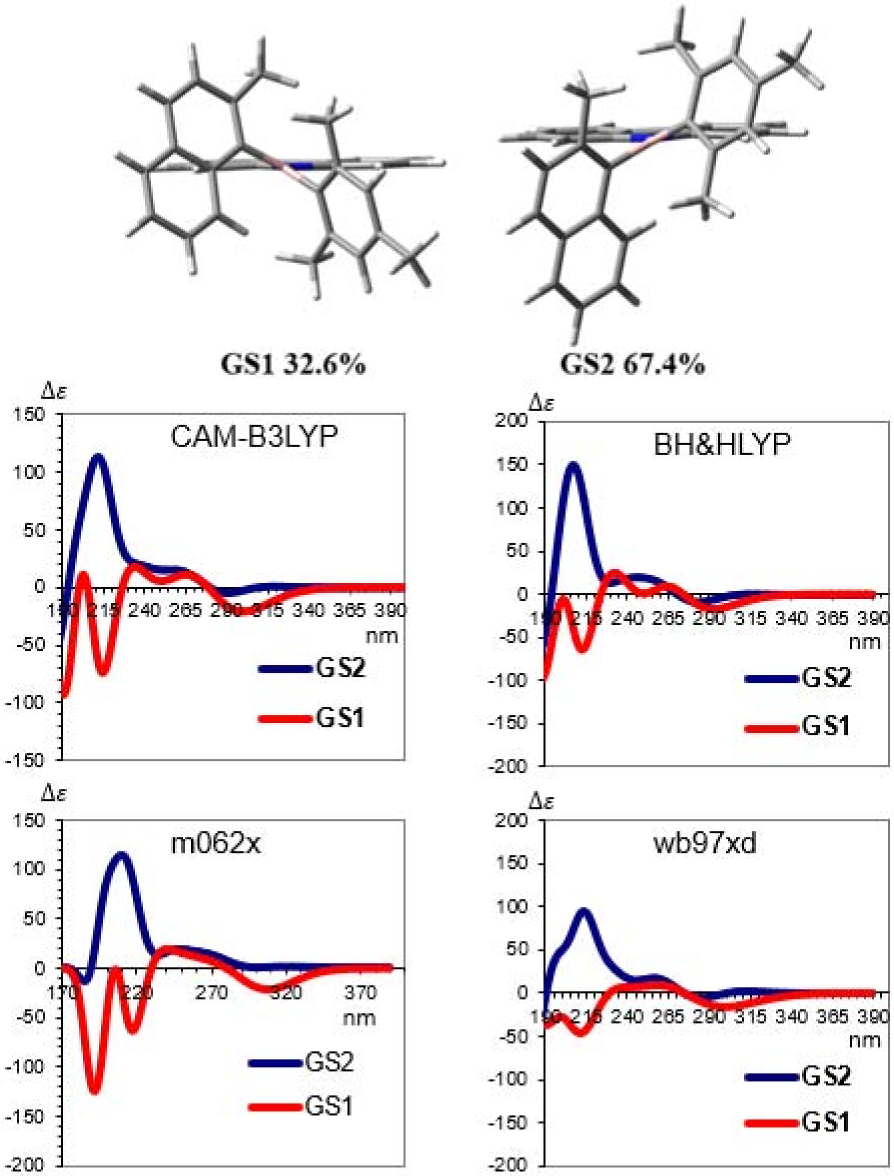


Figure 20 GS1 and GS2 simulated ECD spectra, calculated with 4 different functionals

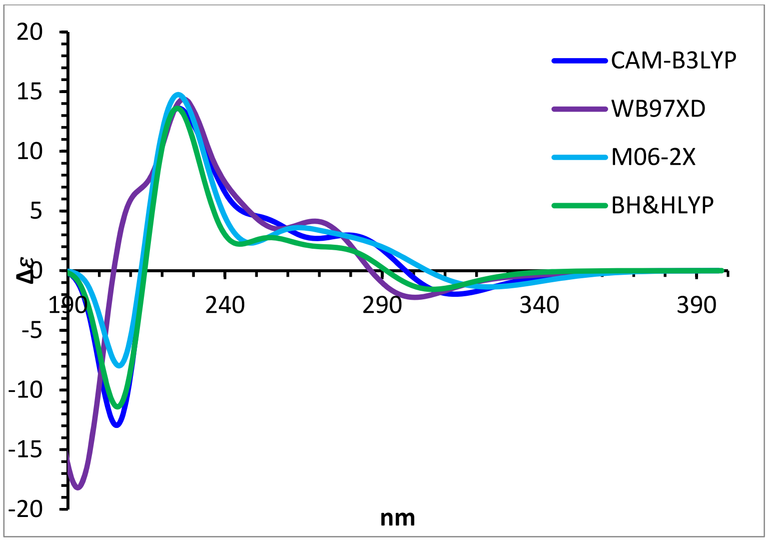


Figure 21 Superimposed ECD spectra calculated with 4 functionals and averaged by Boltzmann equation

Comparing the ECD calculated for *M* atropisomer and the ECD experimental of first eluted peak on CSP-HPLC, we can affirm that they are comparable. This leading us to conclude that the first eluted atropisomer has the *M* absolute configuration (Figure 22).

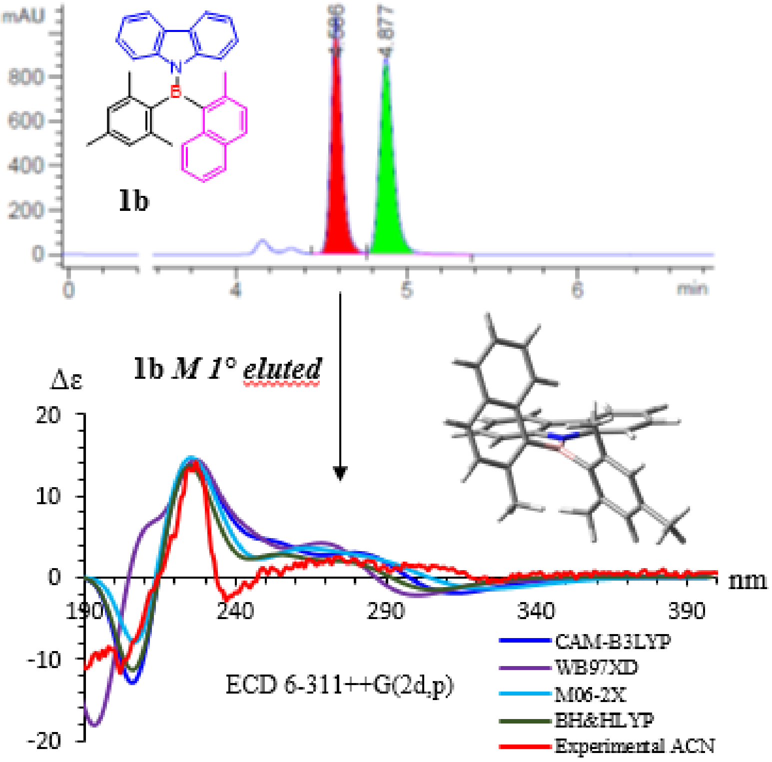


Figure 22 Compound **1b**: experimental and simulated ECD spectra of the first eluted enantiomer.

Fluorescence characterization

In Table 2, Table 3 and Table 4, the calculated values of emission wavelengths, absorption wavelengths and Stokes shift are reported for compounds **1c**, **1a** and **1b**, respectively.

Compound		solvent	Emission wavelength (nm)	Absorption wavelength (nm)	Stokes shift (nm)
1c	GS1	HEX	445	363	82
		THF	449	363	86
		ACN	450	363	87

Table 2 Emission wavelengths, absorption wavelengths and Stokes shift calculated in three different solvents for compound **1c.**

Compound		solvent	emission wavelength (nm)	absorption wavelength (nm)	Stokes shift (nm)
1a	GS1	HEX	473	305	168
		THF	540	303	237
		ACN	572	302	270
	GS2	HEX	441	295	147
		THF	493	294	199
		ACN	517	293	223

Table 3 Emission wavelengths, absorption wavelengths and Stokes shift calculated in three different solvents for compound **1a.**

Compound		solvent	Emission wavelength (nm)	Absorption wavelength (nm)	Stokes shift (nm)
1b	GS1	HEX	433	306	127
		THF	472	305	167
		ACN	489	304	185
	GS2	HEX	427	299	128
		THF	449	298	151
		ACN	457	297	161

Table 4 Emission wavelengths, absorption wavelengths and Stokes shift calculated in three different solvents for compound **1b.**

From Table 2, Table 3 and Table 4, a positive solvatochromic effect in emission for all the compounds is observed. The positive solvatochromic effect can be explained by the TICT character of the excited states.

From steps 4 and 6 of the cycle of fluorescence (see experimental section for more detail), it is possible to calculate the molecular orbital involved in vertical transition with the highest probability (P) (Table 5).

Comp.		**Vertical absorption**	**$\Delta E^{vert\text{-}abs}$ Calc. (eV)**	**Vertical emission**	**$\Delta E^{vert\text{-}emi}$ Calc. (eV)**	**Orbitals involved**
1a	GS1	MO 112 → 113 (P=88%)	4.10	MO 112 → 113 (P=92%)	2.30	HOMO-LUMO
	GS2	MO 112 → 113 (P=87%)	4.10	MO 112 →113 (P=92%)	2.52	HOMO-LUMO
1b	GS1	MO 116→ 117 (P=91%)	4.07	MO 116 →117 (P=91%)	2.63	HOMO-LUMO
	GS2	MO 116→ 117 (P=89%)	4.16	MO 116→ 117 (P=91%)	2.76	HOMO-LUMO
1c	GS1	MO 125→ 126 (P=97%)	3.42	MO 125 →126 (P=98%)	2.76	HOMO-LUMO

Table 5 reported the correspondence between $\Delta E^{vert\text{-}abs}$, $\Delta E^{vert\text{-}emi}$ calculated in steps 4 and 6 and their respective higher probability electronic transitions for all the compound in THF solvent.

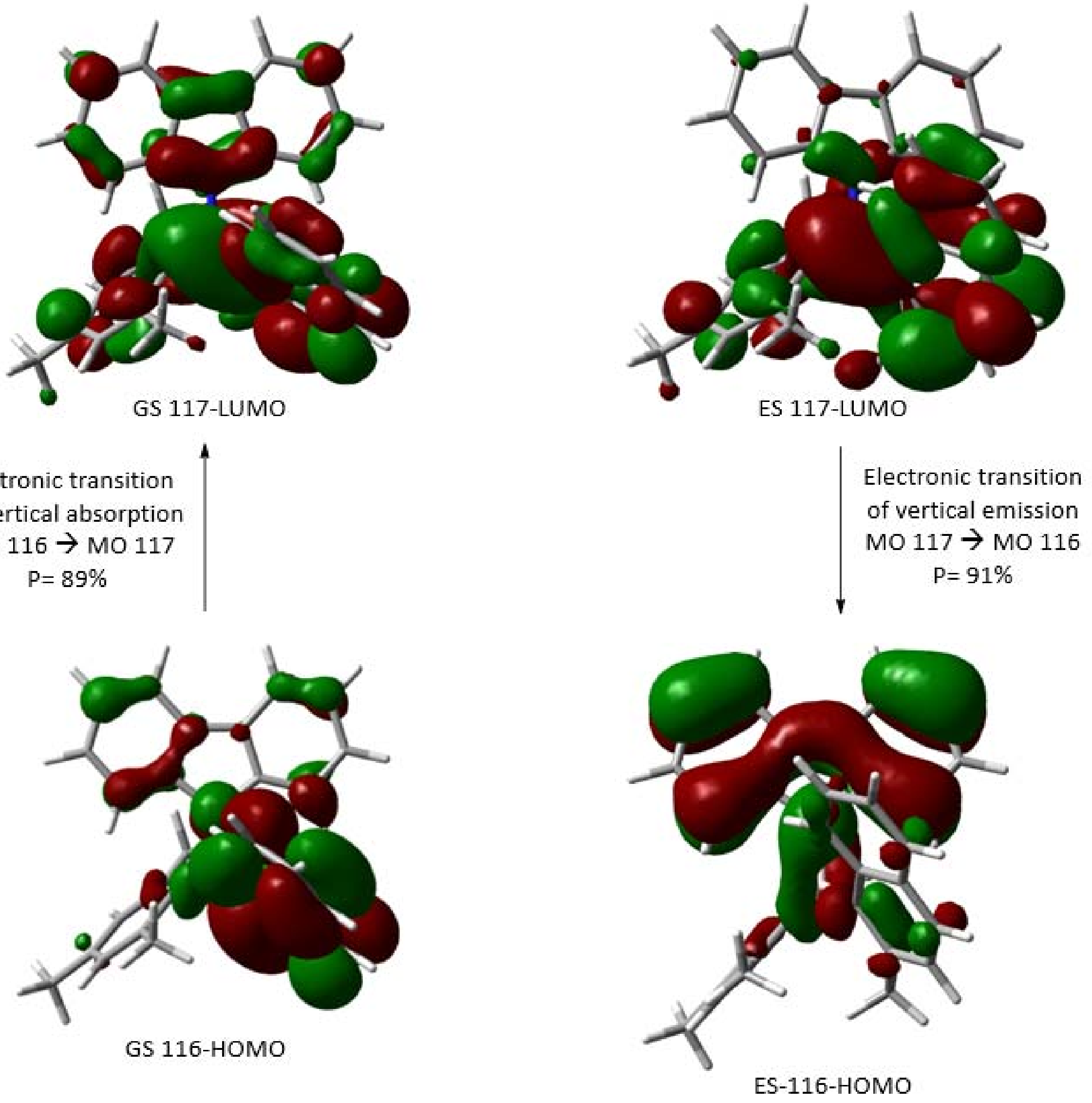
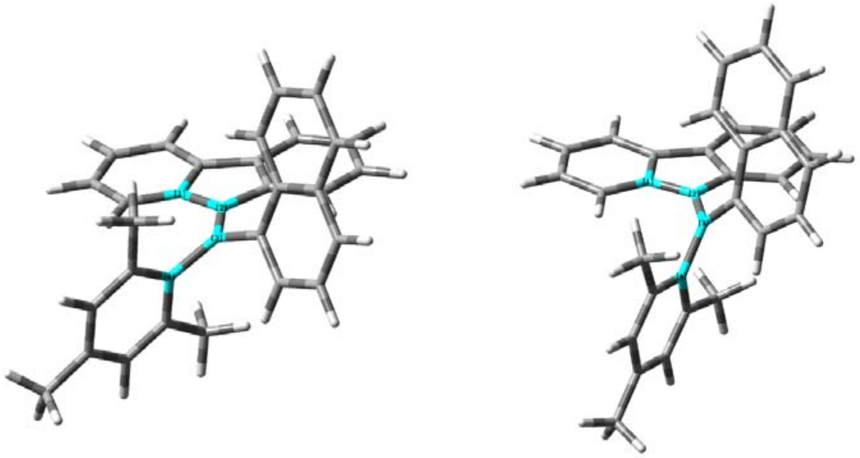


Figure 23 Compound 1b: representation of the HOMO (116) and LUMO (117) calculated orbitals of GS^{eq} and ES^{eq} involved with the highest probability in vertical absorption and emission transitions. It is shown the GS2 conformation and using THF as solvent.

As reported in Table 5, the orbitals involved in vertical transitions of absorption and emission are HOMO-LUMO orbitals of the GS^{eq} and ES^{eq}. The graphic analysis of these orbitals has highlighted that during the vertical transitions they are localized in two different regions of the molecules: the carbazole side (donor group) and the bis-aryl-boron side (acceptor group) (Figure 23).

Moreover, it is possible to analyze the variation of the dihedral angle C-B-N-C (θ) in the geometries of the GS^{eq} and ES^{eq} (Table 6 and Figure 24).



1a GS2
θ (GS^{eq}) =58.9°

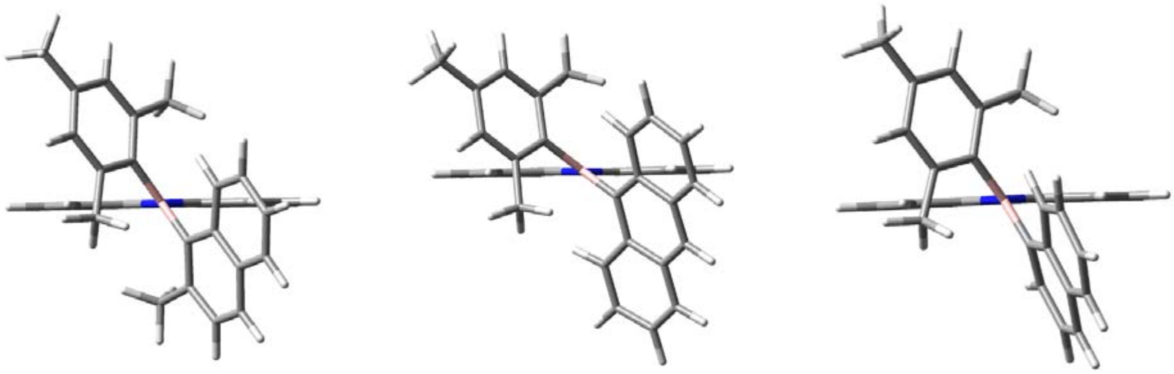
1a GS2
θ (ES^{eq}) =24.5°

Figure 24 optimized GS2 geometries of **1a** in THF with C-B-N-C dihedral angle (θ) labelled

Compound		**Solvent**	**$\Delta\theta^{ESeq\ -GSeq}$ (°)**
1a	GS1	HEX	32.8
		THF	**29.4**
		ACN	27.9
	GS2	HEX	45.6
		THF	**34.4**
		ACN	33.0
1b	GS1	HEX	27.3
		THF	**25.2**
		ACN	23.7
	GS2	HEX	28.4
		THF	**24.6**
		ACN	22.6
1c	GS1	HEX	5.8
		THF	**5.7**
		ACN	5.6

Table 6 $\Delta\theta^{GSeq\ -ESeq}$ values calculated in three different solvents for compounds **1a**, **1b** and **1c**

For all the compound, GSeq and ESeq optimized geometries shows different of C-B-N-C (θ) dihedral angles. This means that during the excited state the molecule relax in a non-radiative way with rotation of the B-N bond. The lower Stokes shift for compound **1c** compared to compounds **1a** and **1b** with the same solvent can be explained by considering the difference in geometry between the molecules in GS^{eq} and ES^{eq}, expressed as a function of the difference in dihedral angle C-B-N-C ($\Delta\theta^{ESeq\text{-}GSeq}$). As reported in Table 6 the difference in the dihedral angle for compound **1c** is smaller than the others (Figure 25). This is due to the geometry of ES^{eq} with a lower perpendicularity caused by the steric bulk given by anthracene. The smaller difference in geometry between the GSeq and the ESeq reduces the extent of non-radiative relaxation in the ES and then the value of the Stokes Shift. The same reasoning can be applied to compound **1b** versus **1a**. Compound **1a** bearing naphthyl substituent has the least steric constraints and therefore the greatest degrees of freedom. Compound **1a** in fact has the highest values of $\Delta\theta^{ESeq\text{-}GSeq}$ for the two conformers (GS1 and GS2) (Table 6).



1b GS1
$\Delta\theta^{ESeq\text{-}GSeq}$= 24.6°

1c
$\Delta\theta^{ESeq\text{-}GSeq}$= 5.7°

1a GS1
$\Delta\theta^{ESeq\text{-}GSeq}$= 29.4°

Figure 25 ES^{eq} optimized geometries of 1**a GS1**, **1b GS1 and 1c** in THF with the difference of C-B-N-C dihedral angle (θ) in respect of GS^{eq} geometries.

Compound		**Solvent**	**$\Delta E^{vert\text{-}abs}$ (eV)**	**$\Delta E^{vert\text{-}emi}$ (eV)**	**Stokes shift (eV)**
1a	GS1	HEX	4.06	2.62	1.44
		THF	**4.10**	**2.30**	**1.80**
		ACN	4.11	2.17	1.93
	GS2	HEX	4.21	2.81	1.40
		THF	**4.22**	**2.52**	**1.70**

		ACN	4.23	2.40	1.83
1b	GS1	HEX	4.05	2.86	1.19
		THF	**4.06**	**2.63**	**1.43**
		ACN	4.08	2.53	1.55
	GS2	HEX	4.15	2.90	1.25
		THF	**4.16**	**2.76**	**1.40**
		ACN	4.18	2.71	1.47
1c	GS1	HEX	3.41	2.79	0.63
		THF	**3.42**	**2.76**	**0.65**
		ACN	3.42	2.76	0.66

Table 7 $\Delta E^{vert\text{-}abs}$, $\Delta E^{vert\text{-}emi}$ and Stokes shift values for all the products

Polar solvent stabilizes the ES^{eq} lowering its energy while $ES^{no\text{-}eq}$ is not affected by the solvent. This leads to a decrease of $\Delta E^{vert\text{-}emi}$ values and then an increase in emission wavelength. On the other hand, $\Delta E^{vert\text{-}abs}$ (and then absorption wavelength) has a small dependence on the polarity of the solvent because even $GS^{no\text{-}eq}$ does not possess geometries and solvation of equilibrium, while GS^{eq} has less charge separation (minor dipole moment) than ES^{eq} (Table 6). Hence, increasing the polarity of the solvent $\Delta E^{vert\text{-}emi}$ decrease while $\Delta E^{vert\text{-}abs}$ (and then absorption wavelength) remains almost constant leading to larger Stokes shifts (Table 7 and Figure 26).

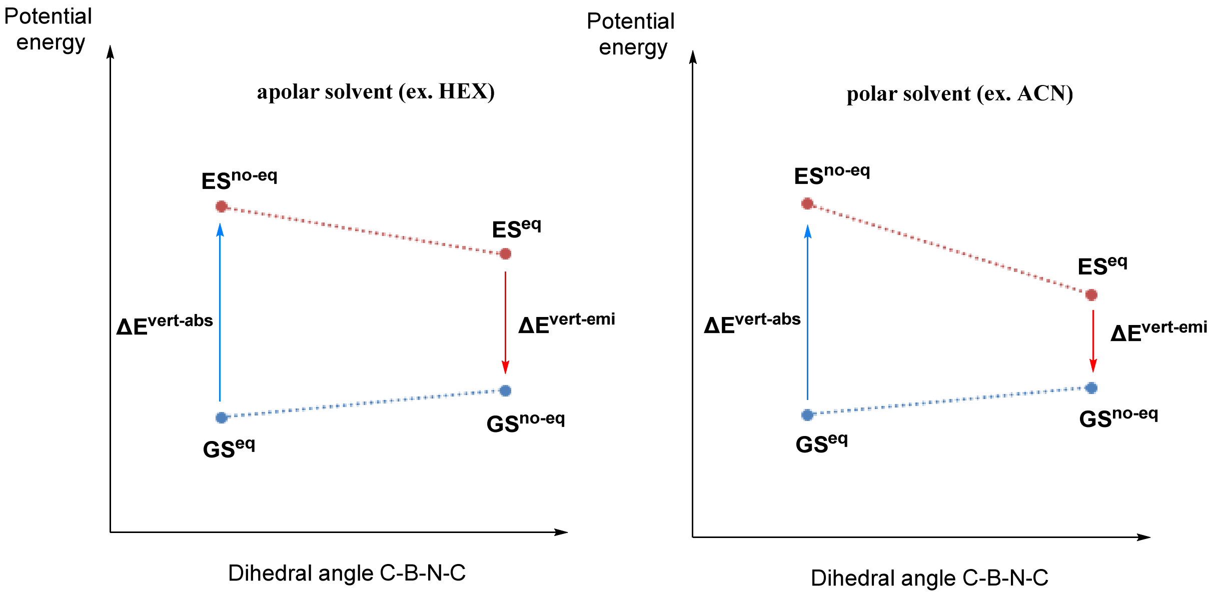


Figure 26 qualitative diagrams of Frank-Condon representing the effect of solvent polarity for the compounds studied

These evidences from calculation confirm the TICT in the excited states from the nitrogen (donor) of the carbazole to the boron (acceptor).

Emission spectra were recorded for compound **1a** (Figure 27), **1b** (Figure 28) and **1c** (Figure 29) with four different solvents (acetonitrile, dichloromethane, n-hexane and THF). The fluorescence spectra were recorded with a wavelength of excitation of 350 nm for all the compound in n-hexane, THF and dichloromethane (DCM) while a wavelength of excitation of 310 nm for acetonitrile.

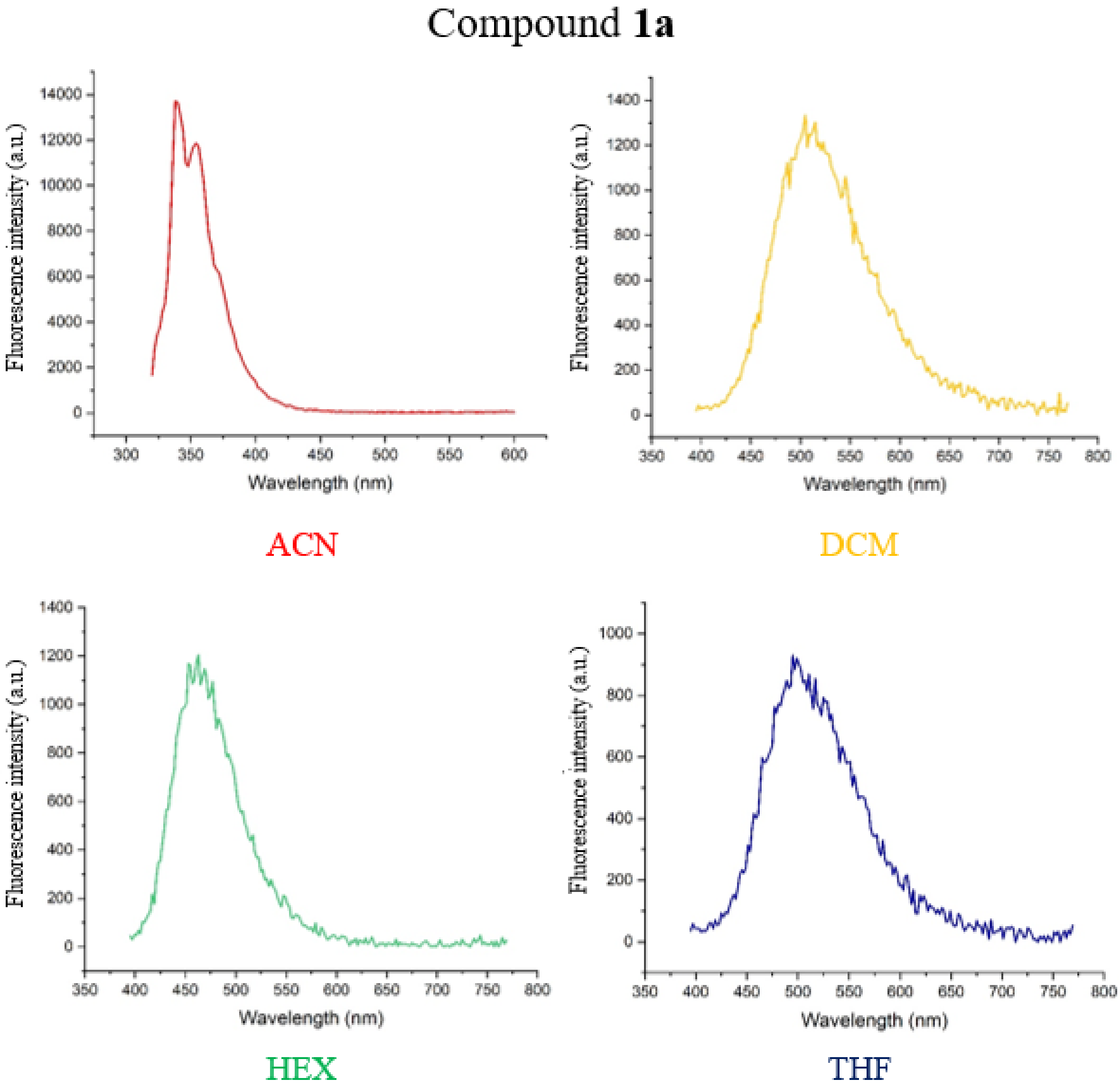
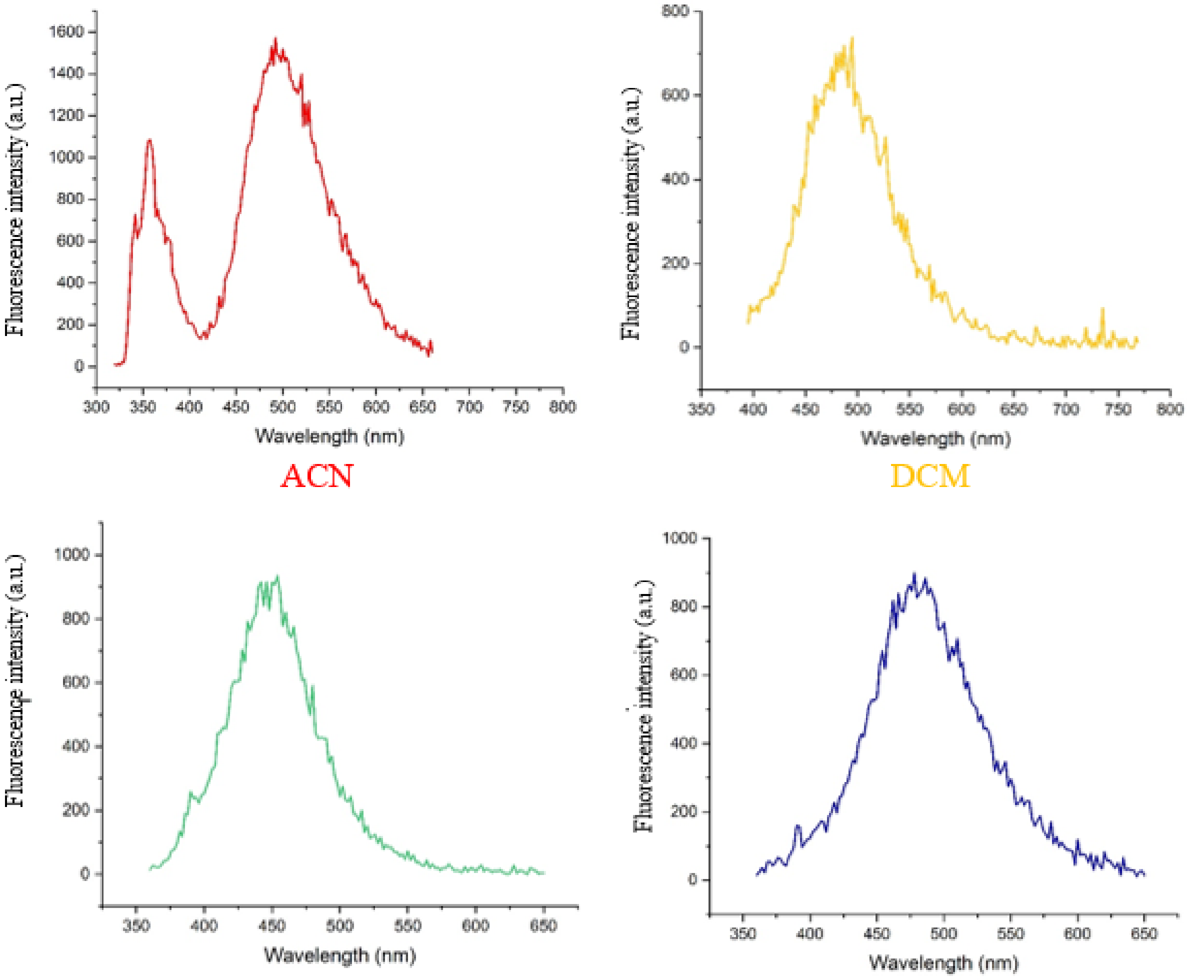


Figure 27 Fluorescence spectra of compound **1a**

Compound **1b**



ACN

DCM

HEX

THF

Figure 28 Fluorescence spectra of compound **1b**

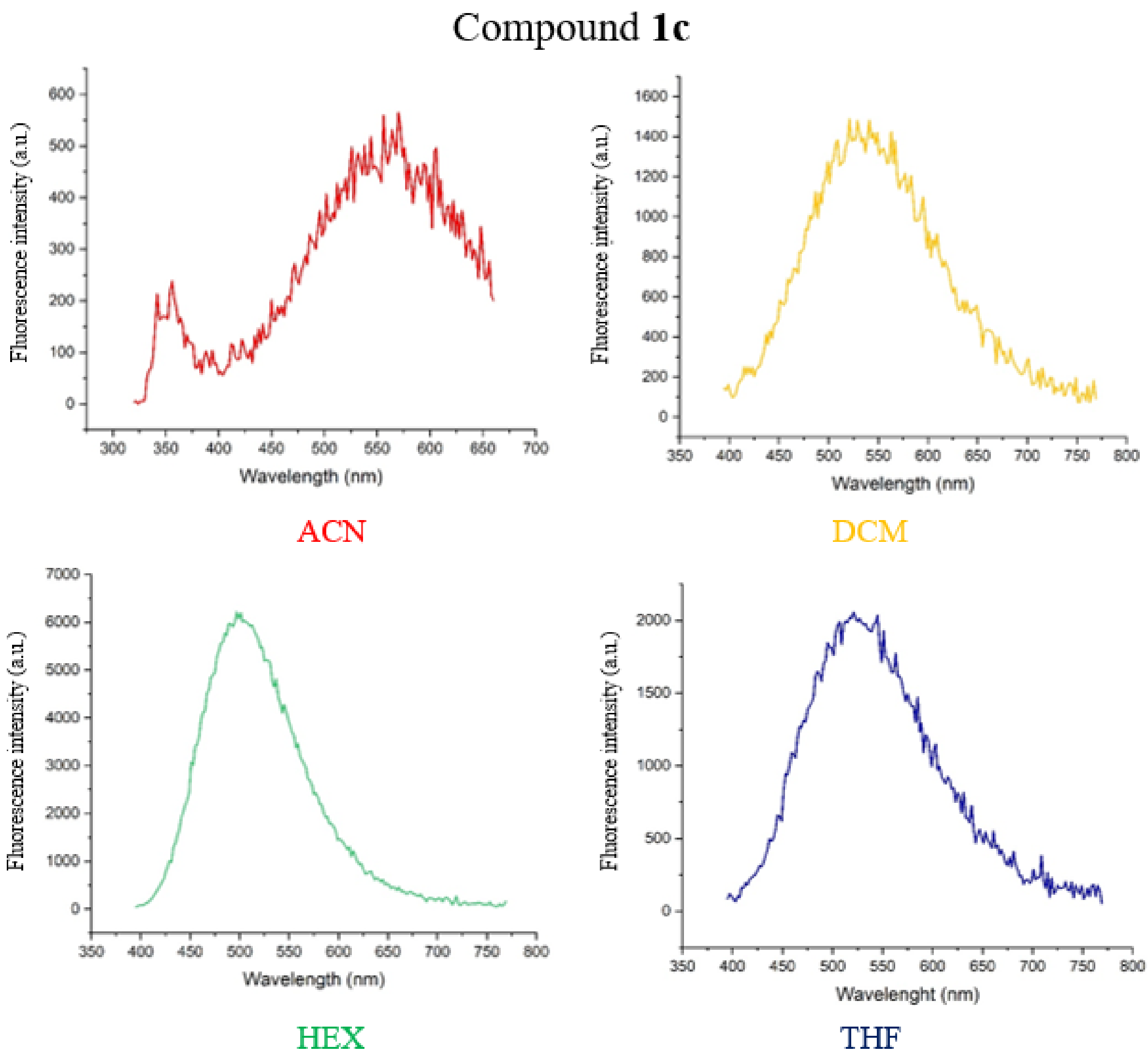


Figure 29 Fluorescence spectra of compound **1c**

This study shows that for the compounds a positive solvatochromic properties with the gradual increase in solvent polarity from hexane to acetonitrile as reported in Table 8. Spectra registered in acetonitrile present discontinuity on this trend probably due to the stability of the compounds in this solvent. Furthermore, from Table 8 are reported the quantum yields and the average lifetime (τ_{ES}) of the excited state.

compound 1a				
Solvent	Emission wavelength (nm)	τ_{ES} (ns)	Quantum Yield (%)	Excitation wavelength (nm)
HEX	465	4	17	350
THF	505	7	19	350
DCM	509	8	29	350

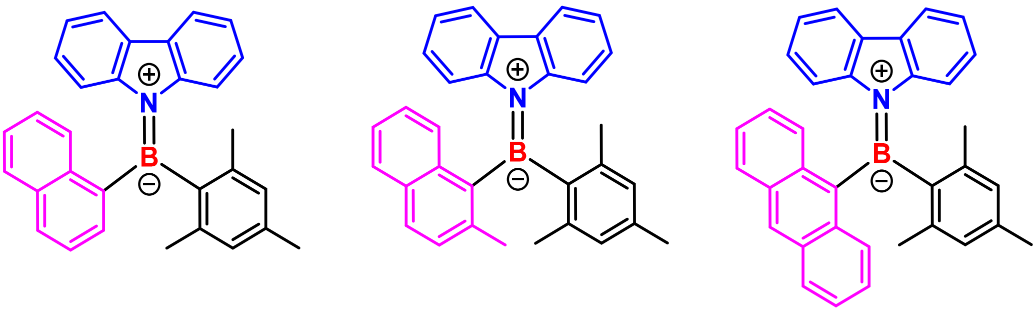
ACN	348	3	26	310
compound 1b				
Solvent	Emission wavelength (nm)	τ_{ES} (ns)	Quantum Yield (%)	Excitation wavelength (nm)
HEX	448	2	6	350
THF	480	3	8	350
DCM	485	3	9	350
ACN	495	5	12	310
compound 1c				
Solvent	Emission wavelength (nm)	τ_{ES} (ns)	Quantum Yield (%)	Excitation wavelength (nm)
HEX	501	7	45	350
THF	525	4	22	350
DCM	535	4	57	350
ACN	564	2	15	310

Table 8 summary of the experimental fluorescence data for all the compounds

From the values of τ_{ES} it is noted that these are of the order of nanoseconds, confirming the the fact that the luminescent emissions are fluorescent.

Conclusions

Our work was focused on improved the general synthesis of carbazole-bis-aryl-boranes **1a**, **1b** and **1c**. A new general synthesis (*path b*) was optimized improving yields and avoiding corrosive reagent (Figure 30).



1a
Yield: 43%

1b
Yield: 73%

1c
Yield: 32%

Figure 30 Summary of the yields obtained following *path b*

Successively, all the conformational behaviors of these molecules have been studied with DFT calculations. Then, with standard kinetic and EXSY analysis, it was possible to obtain the energy barrier of the main transitions (Table 9).

Comp	GS1	GS2	2RF-CC-carb	2RF-CN-mes		2RF-CN-Ar0 2RF-CN-Ar180	
			Calc.	Calc.	Exp.	Calc.	Exp.
1a	1.1	0.0	7.6	21.6	-	20.7 19.9	**20.9**
1b	0.4	0.0	11.4	23.5	**24.6**	26.4 25.3	**26.7**
1c	0.0	-	9.7	22.5	**23.9**	25.6 -	-

Table 9 summary of the results, relative energies in kcal/mol

For compound **1b**, it was possible to separate the atropisomers and assign their absolute configuration comparing the experimental ECD spectrum with a compute one. The first eluted has *M* absolute configuration while the second eluted has the *P*.

Moreover, a positive solvatochromic effect was observed from DFT, TD-DFT calculations of fluorescence for all the products. The solvatochromic effect was explained by confirming the TICT charge transfer in the excited state. The positive solvatochromic effect is also observed in the experimental fluorescence spectra registered by Stagni's research group.

Experimental Section

Instrumentations

Reactions which needed anhydrous conditions were performed under argon flow. The glassware used in these reactions was placed in an oven at +70 °C for at least 1 hour immediately before use.

^{1}H-NMR, ^{13}C-NMR and ^{11}B-NMR spectra were registered with Varian Inova 600 MHz and Varian Mercury 400 MHz spectrometer. Chemical shifts are given in ppm relative to the internal standards tetramethylsilane or relative to the peak of the solvents. The deuterated solvents for NMR spectra were commercially available. Deuterated chloroform was filtered, before use, on aluminium oxide to remove HCl residues.

Silica gel 60 F254 (Merk) for the TLC and silica gel 60 Å (230-400 mesh, Sigma Aldrich) were employed for chromatography separation of the reaction crudes.

HPLC Water^{TM} 600 instrument with detection fixed at 254 nm was used with Enantioselective HPLC columns (DAICEL chiralcel AD-H 5 µm 250 x 21.2 mm, 20 mL/min) to separate stable atropisomers using different mixtures of *n*-hexane and isopropanol as eluent.

Emission spectra were registered with FLS920P- Edinburgh Instruments spectrofluorometer with 10^{-5} M solutions of the sample.

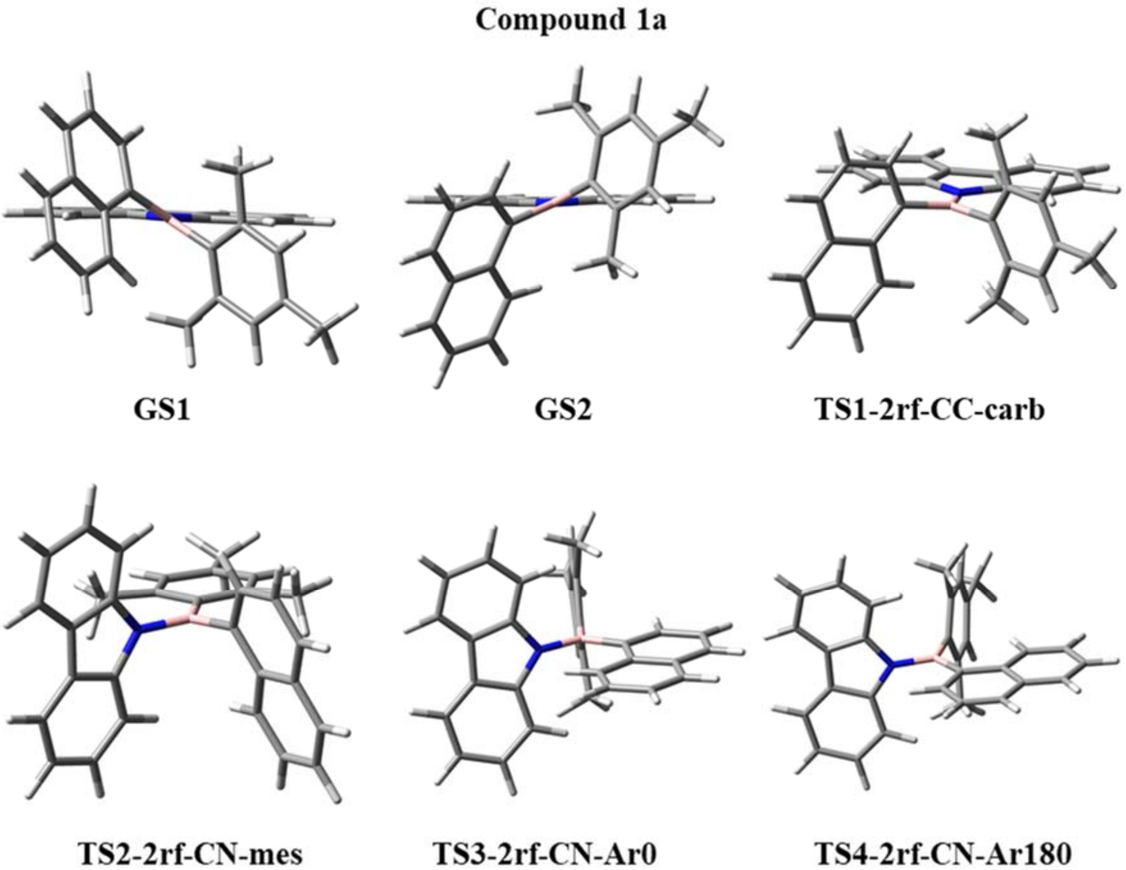
ECD spectra were obtained with JASCO J-810 spectropolarimeter at +25 °C in acetonitrile solution, using a quartz cell with 0.2 cm path length. The concentration of the sample was adjusted to reach about 1.0 in the maximum of absorbance. The spectrum was obtained from the average of 16 scans at 50 nm·min-1 scan rate.

Materials

1-bromo-2-methylnaphthalene, 9-bromoanthracene, 1-bromonaphthalene, 9H-carbazole, mesitylboronic acid, naphthalen-1-ylboronic acid, 1-bromo-2-nitrobenzene were commercially available. THF, ET_2O and Toluene has been dried before use by distillation from Na/benzophenone. 9H-carbazole was re-crystallized in water to obtain as pure one.

Calculations

The calculations for ground states and transition states (Figure 31, Figure 32, Figure 33) employed the B3LYP hybrid HF-DFT method and the 6-311G (d,p) basis sets. The analysis of the vibrational frequencies has shown an absence of imaginary frequency for optimized structure of the ground states, while only one in transition states. Transition states were also validated by visual inspection.



GS1

GS2

TS1-2rf-CC-carb

TS2-2rf-CN-mes

TS3-2rf-CN-Ar0

TS4-2rf-CN-Ar180

Figure 31 Calculate GSs and TSs for compound **1a**

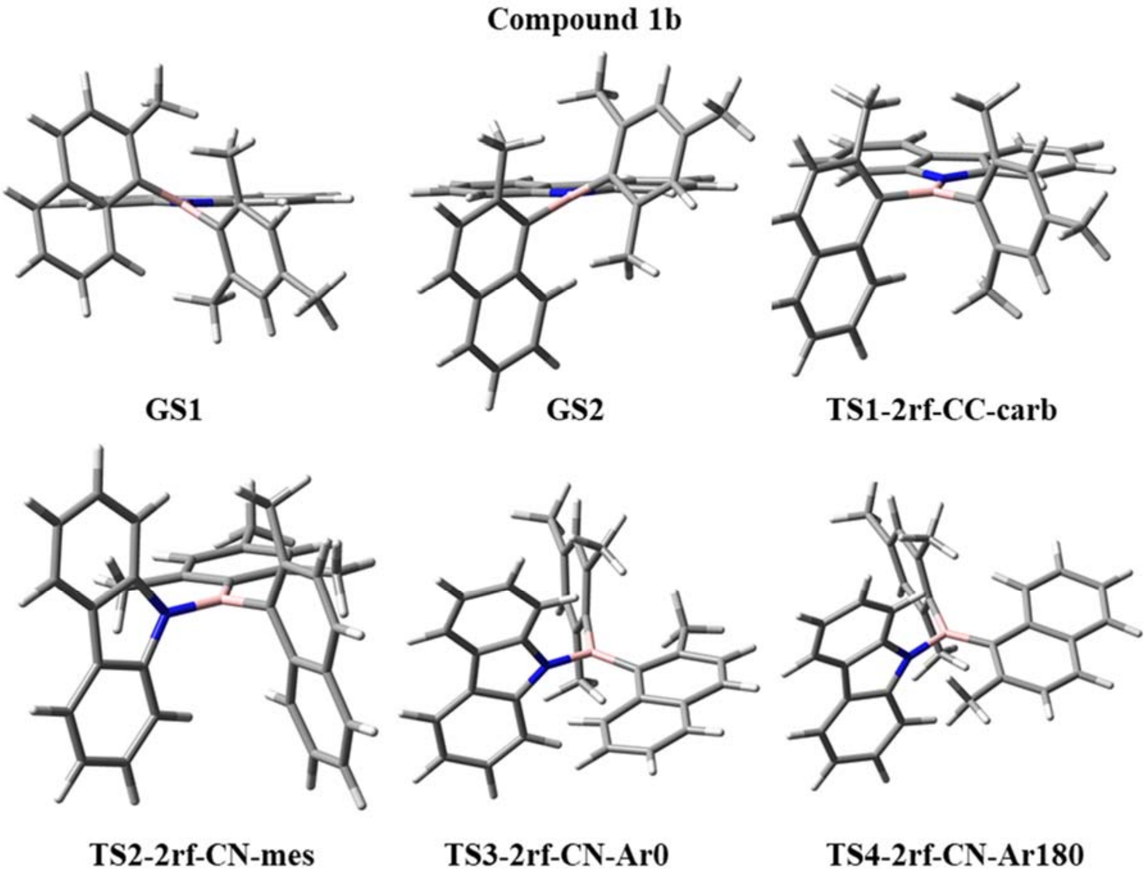


Figure 32 Calculate GSs and TSs for compound **1b**

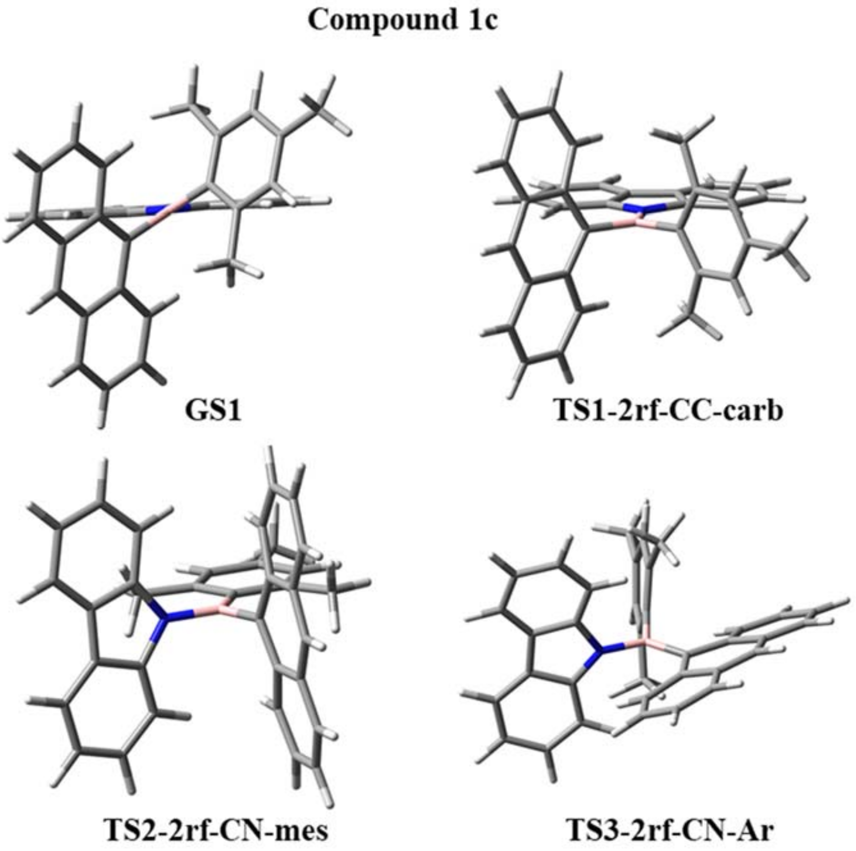


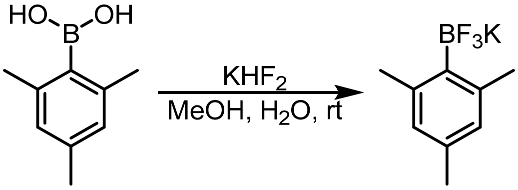
Figure 33 Calculate GSs and TSs for compound **1c**

For the calculation of the florescence cycle, a procedure has been optimized in previous work by the research group was used. The procedure involved 7 steps. The fluorescence data was obtained by the simulation of the cycle based on DFT and TD-DFT. The Functional CAM-B3LYP was used in all the steps. Starting from GS^{eq} geometry, the first step involved an optimization considering solute-solvent interaction with the 6-31G (d) basis sets. In the second step, with 6-31+G(d,p) basis sets, three possible transitions (ESno-eq) were simulated increasing energy from GS^{eq}. The ES$^{no\text{-}eq}$ with the maximum of probability and the minimum of energy was chosen. In the step 3, with and 6-31+G(d,p) basis sets the energy of GSeq was calculated. Therefore, the coordinates of non-equilibrium state of GS^{eq} were saved. In the step 4, the saved coordinates were applied to ES$^{no\text{-}eq}$ choose in step 2 and then the ES$^{no\text{-}eq}$ energy was calculated with 6-31+G(d,p) basis sets. In the step 5, with the 6-31G (d) basis set, the ES$^{no\text{-}eq}$ geometry was optimized reaching the equilibrium state of solvation (ES^{eq}). In the steps 6 and 7 analogously with steps 3 and 4, the vertical emission was calculated with TD-DFT method. In the step 6 were calculated with 6-31+G(d,p) basis set the energy of ES^{eq} and the coordinates of non-equilibrium of ES were saved. In the last step, the coordinates saved in the step 6 were applied to $GS^{no\text{-}eq}$ and then calculate with the same functional and basis set the energy. The geometries of equilibrium in the steps 1 and 5 were calculated in THF and then were used as starting points in the same steps for n-hexane and ACN.

The absolute configuration of the two atropisomers of **1b** was assigned by the simulation of ECD spectrum based on TD-DFT. The theoretical ECD spectra were obtained with four different functionals (CAM-B3LYP,16 ωB97X-D,17 BH&HLYP18 and M06-2x19) with the same 6-311++G(2d,p) basis set, in order to have data redundancy, and to enhance reliability.

Synthesis

Potassium trifluoro(mesityl)borane salt



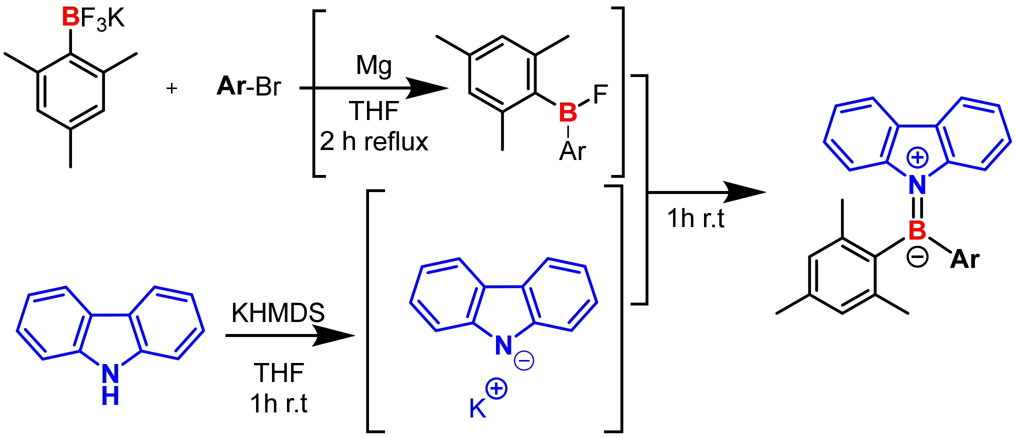
To a solution of mesitylboronic acid (5 g, 30.5 mmol, 1 eq) dissolved in 20 mL of MeOH was added slowly with vigorous stirring a solution of KHF_2 (7.93 g, 101.5 mmol, 3.33 eq) in H_2O (23 mL). The resulting mixture was stirred for 15 min and a white solid was obtained; H_2O was removed as azeotropic mixture with CH_3CN under reduced pressure. The excess of KHF_2 was removed using a Soxhlet extractor. A white solid was obtained after removing CH_3CN under reduce pressure. The yield is almost quantitative.

^{1}H NMR (400 MHz, DMSO-d6) δ = 6.48 (s, 1H), 2.25 (m, 6H), 2.09 ppm (s, 3H).

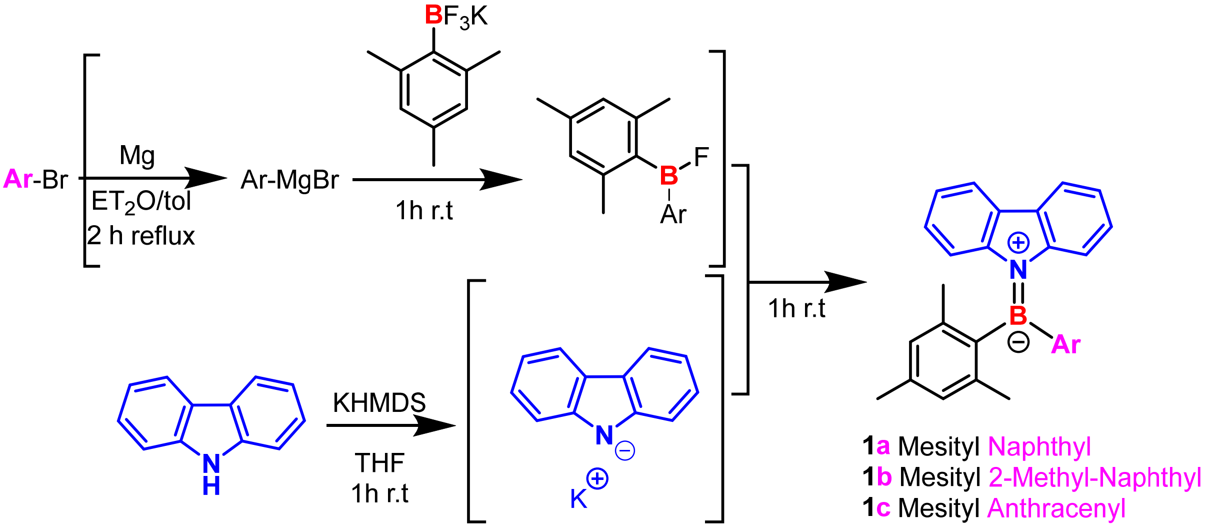
Synthesis of products 1a, 1b and 1c

Product **1b** is prepared following different strategies: *path a* and *path b*. The compounds **1a, 1c** is prepared following *path b*.

Path a



Path b



1a Mesityl Naphthyl
1b Mesityl 2-Methyl-Naphthyl
1c Mesityl Anthracenyl

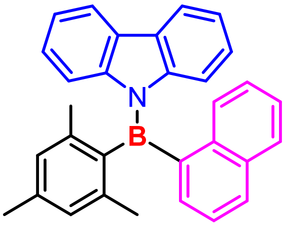
Path a

In a 25 mL oven-dried reaction flask magnesium foil (10 eq), a tip of iodine, MesBF3K (2.4 mmol) and the solvents THF (15 mL) were added. The arylbromine (2.4 mmol) was dropped at room temperature and the resulting solution was stirred under argon at reflux. When the discoloration of iodine was visible, the reaction time was taken for 1 h. After cooling to room temperature, the formation of the Mes-aryl-fluoroborate was checked at ^{19}F NMR. Simultaneously, in another 25 mL oven-dried reaction flask, carbazole (2.4 mmol) in THF (10 mL) was reacted with KHMDS (2.4 mmol) at room temperature. After 1-hour, when MesBF3K salt has been disappeared, the Mes-aryl-fluoroborate solution was dropped to second flask at room temperature. The residue was diluted in DCM and filtered on Celite®, then evaporated the solvent. The products were purified by chromatography separation on silica gel, with eluent *n*-hexane/DCM in 9:1 ratio.

Path b

In a 25 mL oven-dried reaction flask, magnesium slice (10 eq), the solvents Et_2O/toluene (10 mL:5 mL) and a tip of iodine were added. The arylbromine (2.4 mmol) was dropped at room temperature and the resulting solution was stirred under argon at reflux. When the discoloration of iodine was visible, the reaction time was taken for 1 h. After cooling to room temperature, the $MesBF_3K$ (2.4 mmol) was added and the reaction was stirred another 1 h. The formation of the Mes-Aryl fluoro borate was checked at ^{19}F NMR. Meanwhile, in another 25 mL oven-dried reaction flask, carbazole (2.4 mmol) in THF (10 mL) was reacted with KHMDS (2.4 mmol) at room temperature. After 1-hour, when $MesBF_3K$ has been disappeared, the Mes-Aryl fluoro borate solution was dropped to second flask at room temperature. The residue was diluted in DCM and filtered on Celite®, then evaporated the solvent. The products were purified by chromatography separation on silica gel, with eluent *n*-hexane/DCM in 9:1 ratio.

Compound **1a 9-(mesityl(naphthalen-1-yl)boraneyl)-9H-carbazole**



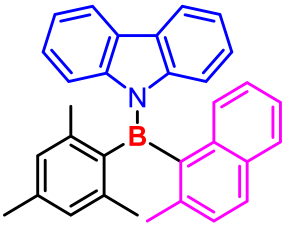
Compound **1a** was synthetized following ***path b*** starting with 1-bromo-naphthalene with 43% of yields.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.63 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.51 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.39 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.11 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 4.9 Hz, 2H), 6.77 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 2.36 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 77 ppm) δ 144.06 (Cq), 142.69 (Cq), 140.58 (Cq-B broden), 140.13 (Cq), 138.73 (Cq), 138.30 (Cq), 134.87 (Cq), 133.16 (CH), 133.01 (Cq), 130.56 (CH), 128.63 (CH), 128.43 (Cq), 128.36 (CH), 128.24 (CH), 128.00 (CH), 126.55 (CH), 126.44 (CH), 125.84 (CH), 125.68 (CH), 125.63 (CH), 122.91 (CH), 122.68 (CH), 119.48 (CH), 119.32 (CH), 116.99 (CH), 115.73 (CH), 22.65 (CH_3), 21.78 (CH_3), 21.38 (CH_3).

^{11}B NMR (192 MHz, CDCL$_3$) δ 51.62.

Compound **1b 9-(mesityl(2-methylnaphthalen-1-yl)boraneyl)-9H-carbazole**



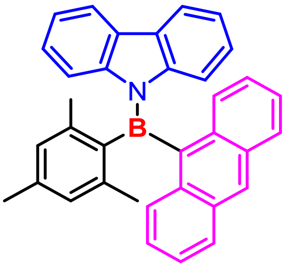
Compound **1b** was synthetized by ***path b*** starting with 1-bromo-2-mehtyl-naphthalene with 73% of yields. Atropisomers were separated with AD-H column and eluent *n*-hexane:*i*-PrOH (97:3) with a flow 20 mL/min.

^{1}H NMR (600 MHz, CD$_2$Cl$_2$, 5.32 ppm) δ 8.02 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.97 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.71 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.20 – 7.10 (m, 4H), 7.03 (dt, *J* = 8.5, 0.9 Hz, 1H), 6.89 (s, 1H), 6.88 – 6.82 (m, 2H), 6.65 – 6.60 (m, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (151 MHz, CD$_2$CL$_2$, 53.3 ppm) δ 143.22 (Cq), 142.79 (Cq), 140.92 (Cq-B broden), 140.77 (Cq-B broden), 139.86 (Cq), 139.56 (Cq), 138.66 (Cq), 138.40 (Cq), 135.49 (Cq), 131.74 (Cq), 129.80 (CH), 129.28 (CH), 128.84 (CH), 128.70 (CH), 128.42 (CH), 128.23 (Cq), 128.11 (Cq), 127.19 (CH), 126.19 (CH), 125.95 (CH), 125.81 (CH), 124.61 (CH), 122.85 (CH), 122.61 (CH), 119.45 (CH), 119.33 (CH), 115.70 (CH), 115.52 (CH), 22.35 (CH$_3$), 21.81 (CH$_3$), 21.44 (CH$_3$), 20.91 (CH$_3$).

^{11}B NMR (192 MHz, CD$_2$CL$_2$) δ 53.77.

Compound **1c 9-(anthracen-9-yl(mesityl)boraneyl)-9H-carbazole**



Compound **1c** was synthetized by ***path b*** starting with 9-bromo-anthracene with 32% of yields.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.56 (s, 1H), 8.01 (dt, *J* = 7.9, 1.9 Hz, 3H), 7.95 (dd, *J* = 8.8, 1.0 Hz, 2H), 7.89 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.16 (dddd, *J* = 7.8, 6.4, 3.8, 1.3 Hz, 3H), 7.10 – 7.02 (m, 2H), 6.83 (s, 2H), 6.60 (ddd, *J* = 8.6, 7.2, 1.3 Hz, 1H), 6.19 – 6.15 (m, 1H), 2.31 (s, 3H), 2.00 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 143.51 (Cq), 142.73 (Cq), 140.91 (Cq), 139.54 (Cq), 138.59 (Cq-B broaden), 134.60 (Cq), 131.32 (Cq), 129.84 (CH), 129.13 (CH), 129.12 (CH), 128.63 (Cq), 128.22 (Cq), 127.95 (CH), 126.37 (CH), 126.07 (CH), 125.87 (CH), 125.02 (CH), 123.07 (CH), 122.62 (CH), 119.62 (CH), 119.30 (CH), 116.41 (CH), 115.90 (CH), 22.64 (CH$_3$), 21.33 (CH$_3$).

^{11}B NMR (192 MHz, CDCl$_3$) δ 55.05.

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```
Compound 1a GS1

 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.95634273
A.U. after    1 cycles
 Lowest frequency =  22.5524

 Zero-point correction=                          0.480493
(Hartree/Particle)
 Thermal correction to Energy=                   0.508064
 Thermal correction to Enthalpy=                 0.509008
 Thermal correction to Gibbs Free Energy=        0.421371
 Sum of electronic and zero-point Energies=          -1276.475850
 Sum of electronic and thermal Energies=             -1276.448279
 Sum of electronic and thermal Enthalpies=           -1276.447335
 Sum of electronic and thermal Free Energies=        -1276.534972

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0        0.096578    0.003873    0.211186
      2          6           0        1.550181    1.573375    2.383269
      3          1           0        0.655768    1.128377    2.827998
      4          1           0        2.297217    0.779122    2.305599
      5          1           0        1.929513    2.321810    3.081928
      6          6           0        0.323039    2.161909   -1.208031
      7          6           0        0.785367    3.465384   -1.399847
      8          1           0        0.601811    3.951829   -2.353730
      9          6           0        1.465657    4.161903   -0.402176
     10          6           0        1.685898    3.510877    0.811576
     11          1           0        2.204587    4.037410    1.607727
     12          6           0        1.264501    2.198983    1.034162
     13          6           0        0.563627    1.501352    0.021675
     14          6           0       -0.429177    1.498114   -2.344291
     15          1           0       -1.504408    1.466942   -2.144610
     16          1           0       -0.282873    2.049929   -3.275060
     17          1           0       -0.106872    0.467992   -2.517626
     18          6           0        1.973297    5.563687   -0.636701
     19          1           0        1.962818    6.151094    0.284596
     20          1           0        3.006057    5.549907   -1.002591
     21          1           0        1.369667    6.087517   -1.381420
     22          7           0       -1.309092   -0.338612    0.097720
     23          6           0       -2.417734    0.509592    0.377581
     24          6           0       -1.858998   -1.574538   -0.351904
     25          6           0       -3.623522   -0.182810    0.134776
     26          6           0       -2.439489    1.809951    0.886187
     27          6           0       -3.268080   -1.502087   -0.342149
     28          6           0       -4.854921    0.431177    0.375060
     29          6           0       -3.675515    2.407927    1.114783
     30          1           0       -1.528536    2.350827    1.093854
     31          6           0       -4.037668   -2.583373   -0.778804
     32          6           0       -4.875401    1.731697    0.860930
     33          1           0       -5.779945   -0.103040    0.188781
     34          1           0       -3.703766    3.420203    1.501915
     35          1           0       -5.120397   -2.525704   -0.767899
     36          1           0       -5.821634    2.224597    1.052206
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     37          6           0       -1.996134   -3.778387   -1.276864
     38          1           0       -1.505043   -4.667936   -1.654828
     39          6           0       -1.214701   -2.710836   -0.845646
     40          1           0       -0.138080   -2.774592   -0.894613
     41          6           0       -3.395411   -3.724894   -1.238392
     42          1           0       -3.975890   -4.573546   -1.581430
     43          6           0        1.119307   -1.134110    0.593585
     44          6           0        2.422655   -1.314254    0.011693
     45          6           0        2.870293   -0.577428   -1.118493
     46          6           0        3.312284   -2.298797    0.557486
     47          6           0        1.654373   -2.885252    2.226419
     48          6           0        4.112278   -0.790043   -1.667866
     49          1           0        2.221764    0.174238   -1.547341
     50          6           0        4.588336   -2.494408   -0.032978
     51          6           0        2.899187   -3.064407    1.677717
     52          1           0        1.341125   -3.474529    3.081013
     53          6           0        4.983481   -1.758242   -1.121785
     54          1           0        4.426816   -0.209515   -2.527958
     55          1           0        5.247483   -3.243941    0.392957
     56          1           0        3.584053   -3.798901    2.089245
     57          1           0        5.960026   -1.917455   -1.565073
     58          6           0        0.771307   -1.935192    1.673278
     59          1           0       -0.210393   -1.822916    2.120893
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```

Compound 1a GS2

```
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.95743337
A.U. after    1 cycles
 Lowest frequency =  24.0210

 Zero-point correction=                           0.480319
(Hartree/Particle)
 Thermal correction to Energy=                    0.508035
 Thermal correction to Enthalpy=                  0.508979
 Thermal correction to Gibbs Free Energy=         0.420667
 Sum of electronic and zero-point Energies=          -1276.477115
 Sum of electronic and thermal Energies=             -1276.449399
 Sum of electronic and thermal Enthalpies=           -1276.448455
 Sum of electronic and thermal Free Energies=        -1276.536766

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0       -0.275633   -0.380493   -0.199794
      2          6           0       -1.439951   -2.061582    2.027863
      3          1           0       -0.999666   -1.200545    2.540659
      4          1           0       -0.612441   -2.696973    1.701296
      5          1           0       -2.021127   -2.619762    2.764453
      6          6           0       -2.655898   -0.441026   -1.225338
      7          6           0       -3.977384   -0.895162   -1.237592
      8          1           0       -4.622951   -0.608008   -2.062873
      9          6           0       -4.491698   -1.697069   -0.220388
     10          6           0       -3.638408   -2.051542    0.825950
     11          1           0       -4.019359   -2.669440    1.634294
     12          6           0       -2.306091   -1.639747    0.860798
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     13          6           0       -1.795416   -0.813434   -0.167152
     14          6           0       -2.190994    0.454694   -2.355727
     15          1           0       -2.107732    1.495646   -2.028313
     16          1           0       -2.898867    0.426326   -3.186596
     17          1           0       -1.212526    0.162004   -2.745611
     18          6           0       -5.916775   -2.192984   -0.262460
     19          1           0       -6.340975   -2.273338    0.741444
     20          1           0       -5.972786   -3.187101   -0.719915
     21          1           0       -6.554049   -1.526898   -0.848526
     22          7           0        0.095020    1.015622   -0.124098
     23          6           0       -0.669403    2.066748    0.465090
     24          6           0        1.265420    1.631124   -0.659467
     25          6           0        0.016191    3.291985    0.325715
     26          6           0       -1.879691    2.010038    1.158607
     27          6           0        1.238346    3.017159   -0.399443
     28          6           0       -0.516128    4.468342    0.857714
     29          6           0       -2.398320    3.193055    1.678523
     30          1           0       -2.414119    1.081373    1.288440
     31          6           0        2.265705    3.845977   -0.855521
     32          6           0       -1.729519    4.414071    1.530813
     33          1           0        0.013529    5.408226    0.749275
     34          1           0       -3.341659    3.160748    2.211793
     35          1           0        2.242348    4.910918   -0.652963
     36          1           0       -2.158808    5.317094    1.949316
     37          6           0        3.315896    1.914932   -1.860675
     38          1           0        4.127645    1.491095   -2.440841
     39          6           0        2.299416    1.075550   -1.414082
     40          1           0        2.323075    0.023989   -1.654950
     41          6           0        3.309039    3.286803   -1.581131
     42          1           0        4.115602    3.913866   -1.943219
     43          6           0        0.796315   -1.522790   -0.399245
     44          6           0        1.973973   -1.696635    0.411632
     45          6           0        2.283380   -0.848419    1.509139
     46          6           0        2.868167   -2.782914    0.136994
     47          6           0        1.450395   -3.500386   -1.694098
     48          6           0        3.403610   -1.051878    2.279150
     49          1           0        1.621753   -0.023810    1.741375
     50          6           0        4.018441   -2.964481    0.948841
     51          6           0        2.584591   -3.662278   -0.940125
     52          1           0        1.230062   -4.183182   -2.507155
     53          6           0        4.284204   -2.119329    1.997136
     54          1           0        3.614375   -0.387342    3.109490
     55          1           0        4.684969   -3.791556    0.726499
     56          1           0        3.274995   -4.473642   -1.147210
     57          1           0        5.165165   -2.268992    2.611103
     58          6           0        0.554091   -2.449152   -1.403255
     59          1           0       -0.352451   -2.365609   -1.993221
 ---------------------------------------------------------------------

Compound 1a TS1-2rf-CC-carb
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.94888260
A.U. after    1 cycles
 Lowest frequency =  -31.4981

 Zero-point correction=                           0.480862
(Hartree/Particle)
 Thermal correction to Energy=                    0.507373
 Thermal correction to Enthalpy=                  0.508317
```

```
Thermal correction to Gibbs Free Energy=         0.424247
Sum of electronic and zero-point Energies=          -1276.468020
Sum of electronic and thermal Energies=             -1276.441510
Sum of electronic and thermal Enthalpies=           -1276.440566
Sum of electronic and thermal Free Energies=        -1276.524636

                        Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
     1          5           0        0.006631    0.215887    0.297266
     2          6           0       -0.577588    1.540743   -2.425450
     3          1           0        0.436240    1.740678   -2.783700
     4          1           0       -0.697093    0.459287   -2.334748
     5          1           0       -1.268796    1.878749   -3.201009
     6          6           0       -1.082297    2.375470    1.286723
     7          6           0       -1.582323    3.672906    1.158589
     8          1           0       -1.898580    4.201318    2.053988
     9          6           0       -1.705193    4.299669   -0.079354
    10          6           0       -1.354248    3.563034   -1.208088
    11          1           0       -1.487454    4.005917   -2.191429
    12          6           0       -0.858461    2.259730   -1.122469
    13          6           0       -0.678856    1.649457    0.141231
    14          6           0       -1.047531    1.780179    2.679078
    15          1           0       -0.122568    2.038937    3.203010
    16          1           0       -1.877489    2.163793    3.277175
    17          1           0       -1.134469    0.691188    2.667527
    18          6           0       -2.204374    5.719267   -0.193465
    19          1           0       -1.372802    6.431120   -0.145961
    20          1           0       -2.721980    5.885990   -1.141199
    21          1           0       -2.892424    5.967580    0.618241
    22          7           0       -0.731852   -1.006946    0.148625
    23          6           0       -2.144657   -1.142779   -0.076637
    24          6           0       -0.216702   -2.347795    0.201201
    25          6           0       -2.483076   -2.507703   -0.167461
    26          6           0       -3.138388   -0.168723   -0.187034
    27          6           0       -1.264939   -3.268577    0.005922
    28          6           0       -3.803502   -2.906720   -0.379714
    29          6           0       -4.452122   -0.582296   -0.398562
    30          1           0       -2.914440    0.882229   -0.111851
    31          6           0       -1.021935   -4.643055    0.005262
    32          6           0       -4.789078   -1.935758   -0.497437
    33          1           0       -4.053334   -3.959486   -0.448529
    34          1           0       -5.227056    0.170756   -0.486123
    35          1           0       -1.835774   -5.343308   -0.145659
    36          1           0       -5.820564   -2.225058   -0.662488
    37          6           0        1.314954   -4.180303    0.390829
    38          1           0        2.326413   -4.540396    0.540489
    39          6           0        1.087158   -2.806006    0.393201
    40          1           0        1.911979   -2.130687    0.544268
    41          6           0        0.275743   -5.096409    0.199896
    42          1           0        0.485780   -6.159767    0.203106
    43          6           0        1.550328    0.221046    0.708958
    44          6           0        2.635665    0.275165   -0.232461
    45          6           0        2.443047    0.086968   -1.627019
    46          6           0        3.980065    0.460932    0.231299
    47          6           0        3.197055    0.428998    2.516653
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     48          6           0        3.491343    0.132740   -2.514894
     49          1           0        1.448527   -0.126534   -1.993227
     50          6           0        5.040024    0.521848   -0.711083
     51          6           0        4.229862    0.547435    1.624354
     52          1           0        3.387371    0.465073    3.583765
     53          6           0        4.805327    0.369372   -2.054975
     54          1           0        3.311152   -0.022860   -3.572738
     55          1           0        6.049385    0.678456   -0.344416
     56          1           0        5.249313    0.688062    1.968184
     57          1           0        5.625862    0.412242   -2.762321
     58          6           0        1.870250    0.270307    2.056119
     59          1           0        1.089307    0.181052    2.799691
 ---------------------------------------------------------------------

Compound 1a TS2-2rf-CN-mes
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.92582172
A.U. after    1 cycles
 Lowest frequency =  -33.9649

 Zero-point correction=                           0.480387
(Hartree/Particle)
 Thermal correction to Energy=                    0.506856
 Thermal correction to Enthalpy=                  0.507801
 Thermal correction to Gibbs Free Energy=         0.423393
 Sum of electronic and zero-point Energies=          -1276.445435
 Sum of electronic and thermal Energies=             -1276.418965
 Sum of electronic and thermal Enthalpies=           -1276.418021
 Sum of electronic and thermal Free Energies=        -1276.502429

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0        0.420650   -0.180473   -0.400506
      2          6           0        3.319425    0.709579   -1.105353
      3          1           0        2.732806    0.965556   -1.986816
      4          1           0        3.144048    1.495024   -0.368645
      5          1           0        4.375071    0.745505   -1.379641
      6          6           0        1.521309   -2.492564    0.160032
      7          6           0        2.656373   -3.286264    0.320256
      8          1           0        2.528931   -4.314783    0.642098
      9          6           0        3.943055   -2.816932    0.071971
     10          6           0        4.075915   -1.509440   -0.387129
     11          1           0        5.067059   -1.135276   -0.622569
     12          6           0        2.982405   -0.664706   -0.566958
     13          6           0        1.651446   -1.121049   -0.261998
     14          6           0        0.210073   -3.200446    0.437222
     15          1           0       -0.487742   -3.124804   -0.396447
     16          1           0        0.402862   -4.259939    0.614539
     17          1           0       -0.296553   -2.807404    1.319917
     18          6           0        5.148778   -3.691277    0.295543
     19          1           0        5.964903   -3.427632   -0.380693
     20          1           0        5.521610   -3.574751    1.319367
     21          1           0        4.908836   -4.747248    0.153915
     22          7           0       -0.970440   -0.654027   -0.041853
     23          6           0       -1.573929   -0.570495    1.217054
     24          6           0       -1.980684   -0.940870   -0.962468
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     25          6           0       -2.973161   -0.776115    1.096507
     26          6           0       -0.989166   -0.369604    2.471178
     27          6           0       -3.233714   -1.018124   -0.302667
     28          6           0       -3.783744   -0.745478    2.234344
     29          6           0       -1.816069   -0.347536    3.588836
     30          1           0        0.080363   -0.250483    2.584283
     31          6           0       -4.385860   -1.327798   -1.030277
     32          6           0       -3.202640   -0.525671    3.476486
     33          1           0       -4.854119   -0.897884    2.148141
     34          1           0       -1.375524   -0.192954    4.567437
     35          1           0       -5.348284   -1.387160   -0.533759
     36          1           0       -3.820150   -0.500003    4.366745
     37          6           0       -3.033800   -1.529168   -3.031167
     38          1           0       -2.967180   -1.749808   -4.090655
     39          6           0       -1.873514   -1.224159   -2.327925
     40          1           0       -0.913185   -1.236844   -2.829580
     41          6           0       -4.282769   -1.571406   -2.394130
     42          1           0       -5.168990   -1.813186   -2.969227
     43          6           0        0.408880    1.328229   -0.912279
     44          6           0        0.677204    2.434360   -0.033544
     45          6           0        1.139698    2.254835    1.298555
     46          6           0        0.508290    3.778698   -0.500967
     47          6           0       -0.131195    2.943056   -2.676476
     48          6           0        1.395749    3.321680    2.125764
     49          1           0        1.313711    1.249846    1.663258
     50          6           0        0.769026    4.860525    0.380810
     51          6           0        0.097628    4.003097   -1.839195
     52          1           0       -0.438790    3.111341   -3.702672
     53          6           0        1.199183    4.642585    1.665850
     54          1           0        1.750002    3.150568    3.136082
     55          1           0        0.625985    5.871904    0.014161
     56          1           0       -0.026709    5.023343   -2.186814
     57          1           0        1.395525    5.479176    2.326872
     58          6           0        0.016653    1.617793   -2.209035
     59          1           0       -0.189720    0.816454   -2.906830
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Compound 1a TS3-2rf-CN-Np0
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.92690737
A.U. after    1 cycles
 Lowest frequency =  -42.2349

 Zero-point correction=                           0.480211
(Hartree/Particle)
 Thermal correction to Energy=                    0.506851
 Thermal correction to Enthalpy=                  0.507796
 Thermal correction to Gibbs Free Energy=         0.423074
 Sum of electronic and zero-point Energies=          -1276.446696
 Sum of electronic and thermal Energies=             -1276.420056
 Sum of electronic and thermal Enthalpies=           -1276.419112
 Sum of electronic and thermal Free Energies=        -1276.503834

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0        0.236447   -0.551598   -0.000056
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      2          6           0        1.872190   -0.984283   -2.568387
      3          1           0        0.864897   -1.404896   -2.529105
      4          1           0        1.799597    0.021571   -2.988837
      5          1           0        2.449857   -1.591686   -3.269121
      6          6           0        2.539015   -0.974493    1.209626
      7          6           0        3.924969   -1.148959    1.187984
      8          1           0        4.449296   -1.256559    2.133597
      9          6           0        4.647627   -1.212208    0.000315
     10          6           0        3.925198   -1.148932   -1.187487
     11          1           0        4.449706   -1.256509   -2.133001
     12          6           0        2.539245   -0.974456   -1.209390
     13          6           0        1.814787   -0.834924    0.000047
     14          6           0        1.871695   -0.984363    2.568494
     15          1           0        0.864412   -1.404978    2.529006
     16          1           0        2.449228   -1.591787    3.269320
     17          1           0        1.799013    0.021477    2.988964
     18          6           0        6.149623   -1.356409    0.000465
     19          1           0        6.499821   -1.893164   -0.884551
     20          1           0        6.636282   -0.374799    0.000895
     21          1           0        6.499584   -1.893812    0.885184
     22          7           0       -0.219653    0.895106   -0.000076
     23          6           0       -0.298361    1.729750   -1.125426
     24          6           0       -0.298769    1.729575    1.125378
     25          6           0       -0.336923    3.088844   -0.720974
     26          6           0       -0.443256    1.388909   -2.473615
     27          6           0       -0.337184    3.088732    0.721126
     28          6           0       -0.438079    4.102539   -1.678188
     29          6           0       -0.547264    2.413356   -3.407993
     30          1           0       -0.507484    0.357783   -2.790196
     31          6           0       -0.438672    4.102275    1.678465
     32          6           0       -0.527963    3.761348   -3.020849
     33          1           0       -0.462256    5.142866   -1.372526
     34          1           0       -0.662704    2.160404   -4.456073
     35          1           0       -0.462740    5.142651    1.372959
     36          1           0       -0.610427    4.536976   -3.773320
     37          6           0       -0.548434    2.412820    3.407969
     38          1           0       -0.664215    2.159703    4.455972
     39          6           0       -0.444098    1.388519    2.473468
     40          1           0       -0.508386    0.357342    2.789871
     41          6           0       -0.529018    3.760872    3.021041
     42          1           0       -0.611745    4.536382    3.773606
     43          6           0       -0.776958   -1.735873   -0.000098
     44          6           0       -2.228863   -1.660390   -0.000155
     45          6           0       -2.962889   -0.444692   -0.000091
     46          6           0       -2.991910   -2.878272   -0.000270
     47          6           0       -0.953093   -4.197086   -0.000254
     48          6           0       -4.339441   -0.432768   -0.000154
     49          1           0       -2.431168    0.492001   -0.000003
     50          6           0       -4.410212   -2.832627   -0.000333
     51          6           0       -2.323648   -4.128010   -0.000319
     52          1           0       -0.448522   -5.156400   -0.000294
     53          6           0       -5.077123   -1.633908   -0.000279
     54          1           0       -4.861572    0.517459   -0.000102
     55          1           0       -4.957869   -3.769335   -0.000423
     56          1           0       -2.920919   -5.034514   -0.000406
     57          1           0       -6.160782   -1.606776   -0.000325
     58          6           0       -0.201285   -3.010276   -0.000146
     59          1           0        0.878980   -3.086807   -0.000109
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Compound 1a TS4-2rf-CN-Np180
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1276.92805367
A.U. after    1 cycles
 Lowest frequency =  -41.3938

 Zero-point correction=                           0.480199
(Hartree/Particle)
 Thermal correction to Energy=                    0.506839
 Thermal correction to Enthalpy=                  0.507783
 Thermal correction to Gibbs Free Energy=         0.423007
 Sum of electronic and zero-point Energies=          -1276.447855
 Sum of electronic and thermal Energies=             -1276.421215
 Sum of electronic and thermal Enthalpies=           -1276.420271
 Sum of electronic and thermal Free Energies=        -1276.505047

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0       -0.190911   -0.159018   -0.000044
      2          6           0       -0.758622    1.423827    2.563690
      3          1           0       -1.094973    0.385842    2.504115
      4          1           0        0.236828    1.429319    3.013906
      5          1           0       -1.432727    1.942763    3.249260
      6          6           0       -0.764923    2.101105   -1.210050
      7          6           0       -1.012991    3.475346   -1.188470
      8          1           0       -1.150721    3.993033   -2.133866
      9          6           0       -1.113008    4.193389    0.000119
     10          6           0       -1.013075    3.475229    1.188641
     11          1           0       -1.150869    3.992822    2.134078
     12          6           0       -0.765021    2.100980    1.210100
     13          6           0       -0.584993    1.388166   -0.000003
     14          6           0       -0.758410    1.424085   -2.563706
     15          1           0       -1.432317    1.943193   -3.249338
     16          1           0        0.237114    1.429464   -3.013757
     17          1           0       -1.094933    0.386146   -2.504284
     18          6           0       -1.335389    5.685760    0.000158
     19          1           0       -0.380246    6.222470   -0.000102
     20          1           0       -1.890012    6.007540   -0.884612
     21          1           0       -1.889543    6.007498    0.885226
     22          7           0        1.294773   -0.496602   -0.000024
     23          6           0        2.132168   -0.520860    1.124696
     24          6           0        2.132237   -0.520758   -1.124695
     25          6           0        3.491307   -0.464017    0.720923
     26          6           0        1.803137   -0.686531    2.473676
     27          6           0        3.491351   -0.463954   -0.720834
     28          6           0        4.509596   -0.494709    1.677926
     29          6           0        2.832541   -0.718973    3.407983
     30          1           0        0.779158   -0.820884    2.790934
     31          6           0        4.509698   -0.494569   -1.677777
     32          6           0        4.175995   -0.607331    3.020836
     33          1           0        5.549075   -0.447337    1.371963
     34          1           0        2.588127   -0.850023    4.456322
     35          1           0        5.549159   -0.447224   -1.371748
     36          1           0        4.955630   -0.635749    3.773166
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     37          6           0        2.832747   -0.718697   -3.407954
     38          1           0        2.588397   -0.849667   -4.456318
     39          6           0        1.803287   -0.686328   -2.473707
     40          1           0        0.779327   -0.820664   -2.791034
     41          6           0        4.176178   -0.607083   -3.020717
     42          1           0        4.955859   -0.635441   -3.773002
     43          6           0       -1.163814   -1.376915   -0.000083
     44          6           0       -2.615933   -1.330798   -0.000075
     45          6           0       -3.369894   -0.128272   -0.000072
     46          6           0       -3.355872   -2.561703   -0.000077
     47          6           0       -1.291384   -3.839799   -0.000127
     48          6           0       -4.746932   -0.139743   -0.000060
     49          1           0       -2.853115    0.818628   -0.000078
     50          6           0       -4.774431   -2.540979   -0.000060
     51          6           0       -2.662624   -3.798537   -0.000103
     52          1           0       -0.767583   -4.788670   -0.000152
     53          6           0       -5.462790   -1.353893   -0.000050
     54          1           0       -5.286538    0.800857   -0.000058
     55          1           0       -5.305893   -3.486953   -0.000059
     56          1           0       -3.241496   -4.716879   -0.000105
     57          1           0       -6.546767   -1.346384   -0.000038
     58          6           0       -0.561624   -2.638369   -0.000114
     59          1           0        0.519129   -2.692818   -0.000122
 ---------------------------------------------------------------------
```

Compound 1b GS1

```
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1316.27847872
A.U. after    1 cycles
 Lowest frequency =  25.6218

 Zero-point correction=                           0.507983
(Hartree/Particle)
 Thermal correction to Energy=                    0.537216
 Thermal correction to Enthalpy=                  0.538160
 Thermal correction to Gibbs Free Energy=         0.447361
 Sum of electronic and zero-point Energies=          -1315.770496
 Sum of electronic and thermal Energies=             -1315.741263
 Sum of electronic and thermal Enthalpies=           -1315.740318
 Sum of electronic and thermal Free Energies=        -1315.831117

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0        0.117008    0.093074    0.219289
      2          6           0        1.530645    1.671654    2.429945
      3          1           0        0.638500    1.242700    2.893898
      4          1           0        2.262963    0.866565    2.335251
      5          1           0        1.934799    2.413129    3.121931
      6          6           0        0.294575    2.290745   -1.156969
      7          6           0        0.729685    3.607462   -1.321046
      8          1           0        0.541553    4.106421   -2.267535
      9          6           0        1.388485    4.301327   -0.308231
     10          6           0        1.618256    3.631738    0.893060
     11          1           0        2.123264    4.153661    1.700838
     12          6           0        1.227059    2.306518    1.089132
     13          6           0        0.543048    1.608924    0.062455
```

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     14          6           0       -0.438688    1.649999   -2.319546
     15          1           0       -1.521470    1.671687   -2.163857
     16          1           0       -0.229809    2.190973   -3.244863
     17          1           0       -0.161757    0.605629   -2.477132
     18          6           0        1.866159    5.717784   -0.514311
     19          1           0        1.837617    6.287944    0.417379
     20          1           0        2.901069    5.732809   -0.873968
     21          1           0        1.255586    6.241598   -1.253342
     22          7           0       -1.263795   -0.290676   -0.001770
     23          6           0       -2.420200    0.513677    0.212525
     24          6           0       -1.739729   -1.558712   -0.442285
     25          6           0       -3.582514   -0.234898   -0.071998
     26          6           0       -2.523197    1.817476    0.702347
     27          6           0       -3.149436   -1.547688   -0.500687
     28          6           0       -4.849316    0.327766    0.099276
     29          6           0       -3.793558    2.363752    0.863261
     30          1           0       -1.647765    2.399923    0.946935
     31          6           0       -3.850900   -2.672895   -0.939934
     32          6           0       -4.949504    1.633034    0.562079
     33          1           0       -5.740272   -0.249777   -0.120642
     34          1           0       -3.883700    3.378314    1.234592
     35          1           0       -4.934287   -2.661910   -0.983264
     36          1           0       -5.924214    2.086608    0.700147
     37          6           0       -1.739164   -3.795399   -1.294805
     38          1           0       -1.193408   -4.674847   -1.617288
     39          6           0       -1.024499   -2.681446   -0.863709
     40          1           0        0.054835   -2.699080   -0.860462
     41          6           0       -3.139341   -3.799865   -1.328921
     42          1           0       -3.666278   -4.682575   -1.672453
     43          6           0        1.172146   -1.019486    0.626213
     44          6           0        2.393170   -1.213233   -0.117462
     45          6           0        0.959523   -1.787784    1.773096
     46          6           0        2.685114   -0.496827   -1.311416
     47          6           0        3.355758   -2.183455    0.312014
     48          6           0        1.937714   -2.727752    2.191376
     49          6           0        3.842670   -0.714068   -2.020736
     50          1           0        1.987026    0.248059   -1.665787
     51          6           0        4.542238   -2.386295   -0.439073
     52          6           0        3.094261   -2.927330    1.487931
     53          1           0        1.753735   -3.299311    3.095620
     54          6           0        4.785861   -1.668932   -1.583443
     55          1           0        4.033182   -0.145444   -2.924174
     56          1           0        5.255082   -3.126833   -0.090699
     57          1           0        3.825118   -3.655888    1.824100
     58          1           0        5.694791   -1.832479   -2.151335
     59          6           0       -0.283398   -1.690190    2.633457
     60          1           0       -1.024940   -2.435507    2.325910
     61          1           0       -0.037619   -1.889738    3.679484
     62          1           0       -0.769603   -0.716874    2.585086
 ---------------------------------------------------------------------

Compound 1b GS2
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1316.27841809
A.U. after    1 cycles
 Lowest frequency =  26.6137

 Zero-point correction=                           0.507816
(Hartree/Particle)
```

```
Thermal correction to Energy=                    0.537189
Thermal correction to Enthalpy=                  0.538133
Thermal correction to Gibbs Free Energy=         0.446609
Sum of electronic and zero-point Energies=          -1315.770602
Sum of electronic and thermal Energies=             -1315.741229
Sum of electronic and thermal Enthalpies=           -1315.740285
Sum of electronic and thermal Free Energies=        -1315.831809

                        Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
     1          5           0       -0.262781   -0.338111   -0.229466
     2          6           0       -1.366113   -2.266517    1.872109
     3          1           0       -0.776729   -1.519914    2.409928
     4          1           0       -0.657222   -2.962148    1.416299
     5          1           0       -1.949218   -2.819580    2.611052
     6          6           0       -2.724476   -0.179378   -1.054494
     7          6           0       -4.064701   -0.569727   -1.008217
     8          1           0       -4.755653   -0.154684   -1.736617
     9          6           0       -4.542229   -1.466133   -0.054374
    10          6           0       -3.628939   -1.983294    0.863895
    11          1           0       -3.978002   -2.677185    1.623313
    12          6           0       -2.275569   -1.642747    0.835023
    13          6           0       -1.796996   -0.718535   -0.126869
    14          6           0       -2.327734    0.828803   -2.114157
    15          1           0       -2.279431    1.839482   -1.697313
    16          1           0       -3.062635    0.842277   -2.921856
    17          1           0       -1.352860    0.618393   -2.556463
    18          6           0       -5.991147   -1.887548   -0.033715
    19          1           0       -6.334055   -2.086484    0.984545
    20          1           0       -6.140140   -2.805799   -0.612735
    21          1           0       -6.636454   -1.119810   -0.466650
    22          7           0        0.142147    1.050676   -0.153870
    23          6           0       -0.557867    2.112808    0.492109
    24          6           0        1.313082    1.637213   -0.720682
    25          6           0        0.151265    3.321617    0.329124
    26          6           0       -1.719955    2.076222    1.265608
    27          6           0        1.331632    3.021951   -0.452874
    28          6           0       -0.318510    4.504430    0.904210
    29          6           0       -2.175914    3.264893    1.829220
    30          1           0       -2.263695    1.157769    1.426242
    31          6           0        2.364275    3.826819   -0.938783
    32          6           0       -1.489843    4.472039    1.649184
    33          1           0        0.228958    5.431562    0.776276
    34          1           0       -3.081731    3.247819    2.424628
    35          1           0        2.374896    4.890871   -0.730527
    36          1           0       -1.869912    5.380154    2.102790
    37          6           0        3.338993    1.872535   -1.973769
    38          1           0        4.126823    1.428913   -2.571916
    39          6           0        2.315516    1.057073   -1.499483
    40          1           0        2.313739    0.002862   -1.730044
    41          6           0        3.371275    3.244497   -1.696675
    42          1           0        4.181961    3.852528   -2.081291
    43          6           0        0.832367   -1.473289   -0.418358
    44          6           0        1.866044   -1.639483    0.576736
    45          6           0        0.796619   -2.357403   -1.498453
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     46          6           0        1.978435   -0.797689    1.719858
     47          6           0        2.823899   -2.697208    0.451556
     48          6           0        1.768742   -3.385130   -1.610736
     49          6           0        2.961012   -0.985274    2.662370
     50          1           0        1.279786    0.017766    1.851110
     51          6           0        3.826768   -2.867972    1.441607
     52          6           0        2.747989   -3.557224   -0.669596
     53          1           0        1.724716   -4.049611   -2.467494
     54          6           0        3.898818   -2.032149    2.526876
     55          1           0        3.017597   -0.320871    3.517401
     56          1           0        4.538754   -3.678279    1.321645
     57          1           0        3.475780   -4.355879   -0.771383
     58          1           0        4.668937   -2.170405    3.277280
     59          6           0       -0.215110   -2.239296   -2.618295
     60          1           0       -1.236082   -2.172131   -2.240945
     61          1           0       -0.156985   -3.102681   -3.283833
     62          1           0       -0.032025   -1.348527   -3.228763
 ---------------------------------------------------------------------

Compound 1b TS1-2rf-CC-carb
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1316.26419669
A.U. after    1 cycles
 Lowest frequency =  -44.2319

 Zero-point correction=                           0.508394
(Hartree/Particle)
 Thermal correction to Energy=                    0.536434
 Thermal correction to Enthalpy=                  0.537378
 Thermal correction to Gibbs Free Energy=         0.450529
 Sum of electronic and zero-point Energies=          -1315.755802
 Sum of electronic and thermal Energies=             -1315.727763
 Sum of electronic and thermal Enthalpies=           -1315.726818
 Sum of electronic and thermal Free Energies=        -1315.813668

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0       -0.110530   -0.141289    0.260742
      2          6           0       -0.961151   -1.486762   -2.414443
      3          1           0       -1.813796   -0.832115   -2.605250
      4          1           0       -0.054161   -0.881495   -2.470528
      5          1           0       -0.915331   -2.212932   -3.229193
      6          6           0       -0.593092   -2.533655    1.255393
      7          6           0       -1.165758   -3.806039    1.176325
      8          1           0       -1.144043   -4.440136    2.058591
      9          6           0       -1.732726   -4.294094    0.003811
     10          6           0       -1.645708   -3.483982   -1.124888
     11          1           0       -2.008400   -3.862531   -2.076550
     12          6           0       -1.082028   -2.206302   -1.088244
     13          6           0       -0.592169   -1.671703    0.131013
     14          6           0        0.078733   -2.182554    2.565903
     15          1           0       -0.628106   -1.770187    3.289328
     16          1           0        0.510983   -3.080259    3.014221
     17          1           0        0.889802   -1.465274    2.438088
     18          6           0       -2.392275   -5.649883   -0.049383
     19          1           0       -3.466509   -5.569671    0.150955
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    20          1           0       -2.278757   -6.111529   -1.033361
    21          1           0       -1.971362   -6.328970    0.695972
    22          7           0        1.258059    0.244719    0.056897
    23          6           0        2.367144   -0.612713   -0.260296
    24          6           0        1.808776    1.568154    0.159133
    25          6           0        3.551295    0.147856   -0.333520
    26          6           0        2.406128   -1.989017   -0.488713
    27          6           0        3.198397    1.525694   -0.068115
    28          6           0        4.774553   -0.456412   -0.627120
    29          6           0        3.634573   -2.578100   -0.781539
    30          1           0        1.517601   -2.596555   -0.444558
    31          6           0        3.967945    2.689240   -0.021727
    32          6           0        4.811594   -1.826411   -0.850468
    33          1           0        5.680097    0.137358   -0.680982
    34          1           0        3.669908   -3.646797   -0.960072
    35          1           0        5.036985    2.646674   -0.197206
    36          1           0        5.751627   -2.314606   -1.080418
    37          6           0        1.961476    3.939063    0.466686
    38          1           0        1.478295    4.887812    0.670530
    39          6           0        1.181207    2.785623    0.424427
    40          1           0        0.118832    2.851184    0.590969
    41          6           0        3.342353    3.898864    0.249134
    42          1           0        3.921995    4.813900    0.288660
    43          6           0       -1.257772    0.921046    0.640702
    44          6           0       -2.068557    1.510805   -0.400471
    45          6           0       -1.601645    1.208018    1.958965
    46          6           0       -1.628058    1.580435   -1.748574
    47          6           0       -3.304525    2.161149   -0.085300
    48          6           0       -2.830265    1.862087    2.255592
    49          6           0       -2.384602    2.177138   -2.731150
    50          1           0       -0.650083    1.193268   -2.000295
    51          6           0       -4.084574    2.732254   -1.122075
    52          6           0       -3.685409    2.277064    1.274830
    53          1           0       -3.084219    2.028787    3.298187
    54          6           0       -3.642361    2.735755   -2.422789
    55          1           0       -2.006633    2.227279   -3.746276
    56          1           0       -5.030162    3.196974   -0.861669
    57          1           0       -4.629806    2.750028    1.523337
    58          1           0       -4.240262    3.190315   -3.204620
    59          6           0       -0.689394    0.960756    3.139248
    60          1           0       -0.496859    1.913576    3.643702
    61          1           0       -1.140693    0.295839    3.881045
    62          1           0        0.276632    0.553220    2.851324
 ---------------------------------------------------------------------

Compound 1b TS2-2rf-CN-mes
 Method: b3lyp/6-311g(d,p)
 SCF Done:  E(RB3LYP) =  -1316.24403875     A.U. after    1 cycles
 Lowest frequency =  -37.4028

 Zero-point correction=                           0.507999
(Hartree/Particle)
 Thermal correction to Energy=                    0.535980
 Thermal correction to Enthalpy=                  0.536924
 Thermal correction to Gibbs Free Energy=         0.449729
 Sum of electronic and zero-point Energies=          -1315.736040
 Sum of electronic and thermal Energies=             -1315.708059
 Sum of electronic and thermal Enthalpies=           -1315.707115
```

```
Sum of electronic and thermal Free Energies=       -1315.794310

                        Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
     1          5           0        0.542626    0.033231    0.243554
     2          6           0        3.028180   -1.723535    0.856203
     3          1           0        2.597019   -1.684109    1.856787
     4          1           0        2.416178   -2.412882    0.274625
     5          1           0        4.026466   -2.156195    0.941919
     6          6           0        2.282219    1.762397   -0.689960
     7          6           0        3.601104    2.125779   -0.961591
     8          1           0        3.788875    3.089015   -1.424745
     9          6           0        4.683823    1.303036   -0.666114
    10          6           0        4.416895    0.068682   -0.079461
    11          1           0        5.246772   -0.591098    0.152514
    12          6           0        3.123099   -0.352962    0.218870
    13          6           0        1.994444    0.489754   -0.079919
    14          6           0        1.246109    2.794594   -1.087087
    15          1           0        0.656236    3.140115   -0.237716
    16          1           0        1.748054    3.663500   -1.516276
    17          1           0        0.546465    2.415797   -1.832842
    18          6           0        6.097073    1.742113   -0.946337
    19          1           0        6.527149    2.234711   -0.067075
    20          1           0        6.738362    0.891886   -1.189266
    21          1           0        6.138118    2.454159   -1.773173
    22          7           0       -0.647985    0.919113   -0.095461
    23          6           0       -1.470597    0.826268   -1.227241
    24          6           0       -1.315216    1.743375    0.819805
    25          6           0       -2.682028    1.531928   -1.006677
    26          6           0       -1.213884    0.246170   -2.473609
    27          6           0       -2.582431    2.119892    0.305666
    28          6           0       -3.653574    1.595236   -2.009029
    29          6           0       -2.191945    0.325920   -3.458454
    30          1           0       -0.274795   -0.241818   -2.689041
    31          6           0       -3.416478    2.964970    1.042397
    32          6           0       -3.409853    0.981739   -3.230139
    33          1           0       -4.581647    2.129644   -1.837367
    34          1           0       -2.000817   -0.123730   -4.426421
    35          1           0       -4.387944    3.249578    0.653019
    36          1           0       -4.153356    1.024102   -4.017543
    37          6           0       -1.704822    3.117323    2.745837
    38          1           0       -1.360217    3.535101    3.685351
    39          6           0       -0.860239    2.274512    2.030771
    40          1           0        0.133204    2.064811    2.400795
    41          6           0       -2.980091    3.450884    2.267920
    42          1           0       -3.615716    4.109648    2.848120
    43          6           0        0.083667   -1.338571    0.932208
    44          6           0       -0.295708   -2.453050    0.098932
    45          6           0       -0.103589   -1.458222    2.304732
    46          6           0        0.085607   -2.537154   -1.266952
    47          6           0       -0.998850   -3.570260    0.651161
    48          6           0       -0.794614   -2.580422    2.838803
    49          6           0       -0.256214   -3.612777   -2.052796
    50          1           0        0.703218   -1.752726   -1.687215
    51          6           0       -1.366103   -4.653034   -0.187489
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    52          6           0       -1.267244   -3.585264    2.042311
    53          1           0       -0.949333   -2.626272    3.912600
    54          6           0       -1.012254   -4.675351   -1.514593
    55          1           0        0.061525   -3.648087   -3.088862
    56          1           0       -1.917590   -5.480241    0.247798
    57          1           0       -1.811299   -4.421884    2.468116
    58          1           0       -1.291163   -5.513803   -2.142663
    59          6           0        0.443903   -0.470414    3.311782
    60          1           0       -0.348695    0.121660    3.776337
    61          1           0        0.958889   -1.009039    4.113835
    62          1           0        1.166476    0.216863    2.869144
 ---------------------------------------------------------------------
```

```
Compound 1b TS3-2rf-CN-2MeNp0
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1316.23895524
A.U. after    1 cycles
 Lowest frequency =  -39.7846

 Zero-point correction=                           0.507745
(Hartree/Particle)
 Thermal correction to Energy=                    0.535883
 Thermal correction to Enthalpy=                  0.536827
 Thermal correction to Gibbs Free Energy=         0.449291
 Sum of electronic and zero-point Energies=          -1315.731211
 Sum of electronic and thermal Energies=             -1315.703072
 Sum of electronic and thermal Enthalpies=           -1315.702128
 Sum of electronic and thermal Free Energies=        -1315.789664

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          5           0       -0.107622    0.600664   -0.189394
      2          6           0       -2.011563    0.819675   -2.603361
      3          1           0       -0.963230    1.111501   -2.703059
      4          1           0       -2.103962   -0.210332   -2.954608
      5          1           0       -2.589338    1.451438   -3.283382
      6          6           0       -2.225502    1.330390    1.189328
      7          6           0       -3.605555    1.515957    1.308482
      8          1           0       -4.012992    1.765955    2.284557
      9          6           0       -4.466404    1.415000    0.219943
     10          6           0       -3.890871    1.174939   -1.025128
     11          1           0       -4.524806    1.156760   -1.907742
     12          6           0       -2.518006    0.979308   -1.184589
     13          6           0       -1.653674    1.004416   -0.063993
     14          6           0       -1.402175    1.559540    2.441101
     15          1           0       -0.361863    1.802423    2.217094
     16          1           0       -1.815041    2.394743    3.013394
     17          1           0       -1.408283    0.683218    3.093367
     18          6           0       -5.958563    1.573051    0.378721
     19          1           0       -6.412622    2.004515   -0.516777
     20          1           0       -6.437839    0.603247    0.552483
     21          1           0       -6.204597    2.215054    1.227958
     22          7           0        0.120147   -0.900115   -0.048455
     23          6           0       -0.057662   -1.858626   -1.055938
     24          6           0        0.158681   -1.598758    1.166781
     25          6           0       -0.219561   -3.146205   -0.481331
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     26          6           0        0.031655   -1.711770   -2.444074
     27          6           0       -0.083217   -2.978673    0.944364
     28          6           0       -0.382477   -4.265192   -1.302768
     29          6           0       -0.126735   -2.839628   -3.242007
     30          1           0        0.248040   -0.753993   -2.896217
     31          6           0       -0.071944   -3.875148    2.016866
     32          6           0       -0.351062   -4.105659   -2.681715
     33          1           0       -0.513335   -5.249450   -0.866372
     34          1           0       -0.057780   -2.736830   -4.319279
     35          1           0       -0.261301   -4.930025    1.850283
     36          1           0       -0.471514   -4.965696   -3.330166
     37          6           0        0.498826   -2.046073    3.495370
     38          1           0        0.757882   -1.699169    4.489595
     39          6           0        0.488882   -1.136525    2.444043
     40          1           0        0.766166   -0.106251    2.614714
     41          6           0        0.204669   -3.402652    3.292465
     42          1           0        0.220740   -4.086832    4.132892
     43          6           0        1.094285    1.593126   -0.325837
     44          6           0        2.495179    1.156072   -0.263642
     45          6           0        0.857668    2.991906   -0.353057
     46          6           0        2.924277   -0.189508   -0.430839
     47          6           0        3.541973    2.116815   -0.059108
     48          6           0        1.924773    3.905478   -0.177105
     49          6           0        4.250496   -0.552526   -0.349895
     50          1           0        2.204176   -0.957097   -0.644475
     51          6           0        4.898884    1.715250    0.041433
     52          6           0        3.213614    3.488182    0.003860
     53          1           0        1.702278    4.966580   -0.177234
     54          6           0        5.255958    0.398836   -0.093203
     55          1           0        4.519134   -1.593247   -0.492754
     56          1           0        5.649982    2.479644    0.211563
     57          1           0        4.007160    4.211600    0.163242
     58          1           0        6.293834    0.094769   -0.021477
     59          6           0       -0.486504    3.655626   -0.568882
     60          1           0       -1.111024    3.626863    0.326269
     61          1           0       -0.331167    4.704779   -0.828157
     62          1           0       -1.061702    3.193574   -1.367263
 ---------------------------------------------------------------------


Compound 1b TS4-2rf-CN-2MeNp180
 Method: b3lyp/6-311g(d,p)
 SCF Done:  E(RB3LYP) =  -1316.24091375     A.U. after    1 cycles
 Lowest frequency =  -41.3991

 Zero-point correction=                           0.507986
(Hartree/Particle)
 Thermal correction to Energy=                    0.536042
 Thermal correction to Enthalpy=                  0.536986
 Thermal correction to Gibbs Free Energy=         0.449402
 Sum of electronic and zero-point Energies=          -1315.732928
 Sum of electronic and thermal Energies=             -1315.704872
 Sum of electronic and thermal Enthalpies=           -1315.703927
 Sum of electronic and thermal Free Energies=        -1315.791512

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
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Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
     1          5           0        0.253018   -0.180748    0.108583
     2          6           0        0.904116    1.246081   -2.542132
     3          1           0        1.263584    0.233934   -2.347739
     4          1           0       -0.000935    1.174408   -3.149974
     5          1           0        1.666245    1.746316   -3.145370
     6          6           0        0.480550    2.234261    1.138281
     7          6           0        0.508805    3.623359    0.998637
     8          1           0        0.499848    4.236126    1.896239
     9          6           0        0.575930    4.242688   -0.246719
    10          6           0        0.686766    3.417244   -1.362201
    11          1           0        0.817898    3.866616   -2.343063
    12          6           0        0.664254    2.024052   -1.264781
    13          6           0        0.497288    1.399450   -0.005193
    14          6           0        0.526087    1.686308    2.549788
    15          1           0        1.194366    2.294176    3.165556
    16          1           0       -0.457937    1.697654    3.023673
    17          1           0        0.905168    0.662316    2.581532
    18          6           0        0.551779    5.745499   -0.379562
    19          1           0        0.984782    6.231789    0.498030
    20          1           0        1.105460    6.078116   -1.260935
    21          1           0       -0.475733    6.111792   -0.481918
    22          7           0       -1.226059   -0.540809    0.057365
    23          6           0       -1.986682   -0.654794   -1.113853
    24          6           0       -2.134983   -0.461338    1.119431
    25          6           0       -3.369708   -0.569081   -0.808495
    26          6           0       -1.568829   -0.928651   -2.420130
    27          6           0       -3.465006   -0.445955    0.624876
    28          6           0       -4.321735   -0.680473   -1.825488
    29          6           0       -2.533769   -1.042158   -3.415402
    30          1           0       -0.525040   -1.076647   -2.657944
    31          6           0       -4.543903   -0.397652    1.511712
    32          6           0       -3.899641   -0.903694   -3.129314
    33          1           0       -5.379138   -0.609182   -1.594866
    34          1           0       -2.219910   -1.256097   -4.431101
    35          1           0       -5.560862   -0.379242    1.135130
    36          1           0       -4.627364   -0.995854   -3.927129
    37          6           0       -2.985535   -0.470683    3.361308
    38          1           0       -2.810680   -0.511293    4.430741
    39          6           0       -1.896819   -0.513391    2.496687
    40          1           0       -0.895583   -0.610435    2.891895
    41          6           0       -4.299995   -0.395725    2.878689
    42          1           0       -5.127560   -0.362543    3.577691
    43          6           0        1.328933   -1.314242    0.191850
    44          6           0        2.766045   -1.014916    0.169326
    45          6           0        0.954498   -2.684507    0.207081
    46          6           0        3.307822    0.295769    0.265802
    47          6           0        3.728743   -2.073488    0.065507
    48          6           0        1.942736   -3.695798    0.111472
    49          6           0        4.663912    0.536415    0.236087
    50          1           0        2.647586    1.138375    0.369279
    51          6           0        5.120160   -1.800933    0.025520
    52          6           0        3.275491   -3.409230    0.022304
    53          1           0        1.620836   -4.730788    0.106568
    54          6           0        5.590194   -0.515636    0.105728
    55          1           0        5.018797    1.557937    0.317921
    56          1           0        5.805427   -2.637720   -0.061577
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    57          1           0        4.003912   -4.209677   -0.062346
    58          1           0        6.654168   -0.310612    0.078420
    59          6           0       -0.455706   -3.227949    0.328326
    60          1           0       -1.051649   -3.037881   -0.565865
    61          1           0       -0.412115   -4.309507    0.467661
    62          1           0       -0.997030   -2.807667    1.174167
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```

```
Compound 1c GS1
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1430.62089770
A.U. after    1 cycles
 Lowest frequency =  24.8358

 Zero-point correction=                           0.526937
(Hartree/Particle)
 Thermal correction to Energy=                    0.557192
 Thermal correction to Enthalpy=                  0.558136
 Thermal correction to Gibbs Free Energy=         0.465026
 Sum of electronic and zero-point Energies=          -1430.093960
 Sum of electronic and thermal Energies=             -1430.063705
 Sum of electronic and thermal Enthalpies=           -1430.062761
 Sum of electronic and thermal Free Energies=        -1430.155871

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
     1          6           0        0.431543   -2.071901   -2.438386
     2          1           0        0.080057   -1.105519   -2.807479
     3          1           0        1.478843   -1.942314   -2.153701
     4          1           0        0.397641   -2.775196   -3.272820
     5          6           0       -1.490668   -2.340195    0.879999
     6          6           0       -1.928209   -3.662562    0.780285
     7          1           0       -2.516919   -4.081211    1.591680
     8          6           0       -1.641523   -4.455930   -0.328591
     9          6           0       -0.880587   -3.890691   -1.351231
    10          1           0       -0.650509   -4.486234   -2.230077
    11          6           0       -0.396235   -2.583880   -1.278747
    12          6           0       -0.704336   -1.774177   -0.156947
    13          6           0       -1.895500   -1.566442    2.119878
    14          1           0       -2.765342   -0.932729    1.922213
    15          1           0       -2.166973   -2.253281    2.924335
    16          1           0       -1.106096   -0.912288    2.495040
    17          6           0       -2.110701   -5.887945   -0.407135
    18          1           0       -2.322468   -6.182309   -1.437898
    19          1           0       -1.345008   -6.571654   -0.023894
    20          1           0       -3.015205   -6.044924    0.184923
    21          7           0       -1.063209    0.793800    0.232340
    22          6           0       -2.429462    0.870124   -0.168408
    23          6           0       -0.780957    2.016218    0.909892
    24          6           0       -2.979456    2.103272    0.242098
    25          6           0       -3.189539   -0.024969   -0.924261
    26          6           0       -1.936232    2.824825    0.939225
    27          6           0       -4.301604    2.429270   -0.068209
    28          6           0       -4.506546    0.314672   -1.221672
    29          1           0       -2.780487   -0.962422   -1.269612
    30          6           0       -1.920280    4.063436    1.584452
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     31          6           0       -5.065013    1.526112   -0.796011
     32          1           0       -4.721586    3.377218    0.249098
     33          1           0       -5.107492   -0.377452   -1.800578
     34          1           0       -2.809791    4.683152    1.604959
     35          1           0       -6.093147    1.761879   -1.045470
     36          6           0        0.385443    3.665840    2.192208
     37          1           0        1.288983    3.998281    2.690482
     38          6           0        0.385294    2.427919    1.556392
     39          1           0        1.272198    1.813034    1.569949
     40          6           0       -0.751573    4.483173    2.205234
     41          1           0       -0.719415    5.441637    2.710374
     42          6           0        1.410558   -0.003605   -0.136234
     43          6           0        2.359778   -0.659913    0.691681
     44          6           0        1.880801    0.889376   -1.139534
     45          6           0        1.980770   -1.558424    1.740645
     46          6           0        3.773333   -0.409090    0.528961
     47          6           0        3.297175    1.116957   -1.308465
     48          6           0        1.006288    1.577412   -2.042807
     49          6           0        2.907298   -2.160444    2.546348
     50          1           0        0.933846   -1.777756    1.891633
     51          6           0        4.711309   -1.056711    1.391102
     52          6           0        4.200881    0.467793   -0.467264
     53          6           0        3.756497    2.001860   -2.332469
     54          1           0       -0.062185    1.436275   -1.955512
     55          6           0        1.483240    2.416205   -3.012080
     56          6           0        4.295488   -1.908489    2.373093
     57          1           0        2.581282   -2.839173    3.326529
     58          1           0        5.767085   -0.851234    1.247499
     59          1           0        5.264208    0.650084   -0.591669
     60          6           0        2.879041    2.636492   -3.162786
     61          1           0        4.825724    2.155641   -2.435526
     62          1           0        0.788601    2.921274   -3.673829
     63          1           0        5.015863   -2.393260    3.022227
     64          1           0        3.238526    3.305259   -3.936570
     65          5           0       -0.145135   -0.300984   -0.012842
 ---------------------------------------------------------------------

Compound 1c TS1-2rf-CC-carb
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1430.60831448
A.U. after    1 cycles
 Lowest frequency =  -32.0870

 Zero-point correction=                           0.527201
(Hartree/Particle)
 Thermal correction to Energy=                    0.556349
 Thermal correction to Enthalpy=                  0.557293
 Thermal correction to Gibbs Free Energy=         0.467963
 Sum of electronic and zero-point Energies=          -1430.081113
 Sum of electronic and thermal Energies=             -1430.051966
 Sum of electronic and thermal Enthalpies=           -1430.051022
 Sum of electronic and thermal Free Energies=        -1430.140352

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.592072   -1.878776   -2.567869
```

```
   2          1           0       -1.151628   -0.942189   -2.524013
   3          1           0        0.385796   -1.665086   -3.004267
   4          1           0       -1.122198   -2.539370   -3.257631
   5          6           0       -0.474883   -2.534972    1.209337
   6          6           0       -0.515453   -3.931414    1.187138
   7          1           0       -0.579056   -4.462946    2.132606
   8          6           0       -0.503616   -4.657974    0.000366
   9          6           0       -0.515858   -3.931635   -1.186540
  10          1           0       -0.579762   -4.463358   -2.131881
  11          6           0       -0.475271   -2.535196   -1.209051
  12          6           0       -0.396879   -1.799143    0.000069
  13          6           0       -0.591267   -1.878206    2.568015
  14          1           0       -1.150485   -0.941440    2.524043
  15          1           0       -1.121554   -2.538446    3.257996
  16          1           0        0.386768   -1.664800    3.004203
  17          6           0       -0.497326   -6.166628    0.000506
  18          1           0       -0.996641   -6.568728   -0.884383
  19          1           0        0.528068   -6.552757    0.000501
  20          1           0       -0.996568   -6.568565    0.885510
  21          7           0       -1.276710    0.715646   -0.000107
  22          6           0       -2.679004    0.398835    0.000006
  23          6           0       -1.203867    2.151246   -0.000228
  24          6           0       -3.435250    1.587960   -0.000033
  25          6           0       -3.323279   -0.839113    0.000138
  26          6           0       -2.503207    2.694881   -0.000181
  27          6           0       -4.830299    1.549873    0.000049
  28          6           0       -4.716648   -0.861082    0.000220
  29          1           0       -2.772872   -1.765194    0.000183
  30          6           0       -2.701082    4.076542   -0.000272
  31          6           0       -5.469543    0.317124    0.000175
  32          1           0       -5.403600    2.470069    0.000015
  33          1           0       -5.222013   -1.820144    0.000321
  34          1           0       -3.704674    4.486696   -0.000229
  35          1           0       -6.552261    0.266219    0.000242
  36          6           0       -0.304885    4.371012   -0.000479
  37          1           0        0.555166    5.030761   -0.000600
  38          6           0       -0.092649    2.994199   -0.000387
  39          1           0        0.913016    2.607704   -0.000440
  40          6           0       -1.593601    4.914134   -0.000419
  41          1           0       -1.725761    5.989941   -0.000492
  42          6           0        1.357801    0.276486   -0.000011
  43          6           0        2.079488    0.417923    1.213862
  44          6           0        2.079510    0.417540   -1.213921
  45          6           0        1.427554    0.626576    2.469813
  46          6           0        3.524359    0.449119    1.213431
  47          6           0        3.524382    0.448736   -1.213461
  48          6           0        1.427606    0.625705   -2.469950
  49          6           0        2.130217    0.785653    3.632743
  50          1           0        0.349468    0.711735    2.486904
  51          6           0        4.222693    0.565270    2.454620
  52          6           0        4.210198    0.403168    0.000000
  53          6           0        4.222739    0.564474   -2.454675
  54          1           0        0.349528    0.710850   -2.487060
  55          6           0        2.130286    0.784367   -3.632930
  56          6           0        3.550284    0.725279    3.632372
  57          1           0        1.602609    0.969624    4.561952
  58          1           0        5.307585    0.553971    2.435658
  59          1           0        5.295831    0.396212    0.000012
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    60          6           0        3.550354    0.724041   -3.632502
    61          1           0        5.307631    0.553199   -2.435688
    62          1           0        1.602694    0.967987   -4.562217
    63          1           0        4.093351    0.832519    4.564532
    64          1           0        4.093439    0.830958   -4.564688
    65          5           0       -0.176822   -0.206196   -0.000010
 ---------------------------------------------------------------------
```

Compound 1c TS2-2rf-CN-mes

```
 Method: b3lyp/6-311g(d,p) SCF Done:  E(RB3LYP) =  -1430.58677999
A.U. after    1 cycles
 Lowest frequency =  -35.0641

 Zero-point correction=                           0.526701
(Hartree/Particle)
 Thermal correction to Energy=                    0.555858
 Thermal correction to Enthalpy=                  0.556803
 Thermal correction to Gibbs Free Energy=         0.466838
 Sum of electronic and zero-point Energies=          -1430.060079
 Sum of electronic and thermal Energies=             -1430.030922
 Sum of electronic and thermal Enthalpies=           -1430.029977
 Sum of electronic and thermal Free Energies=        -1430.119942

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
     1          6           0        2.164328    2.759027    0.045558
     2          1           0        1.543339    2.909078   -0.837913
     3          1           0        1.521427    2.894633    0.915463
     4          1           0        2.913988    3.551985    0.061285
     5          6           0        2.995582   -1.037612    0.037238
     6          6           0        4.384908   -0.919096    0.048423
     7          1           0        4.982910   -1.824587    0.055740
     8          6           0        5.034219    0.312005    0.053289
     9          6           0        4.245828    1.459948    0.053636
    10          1           0        4.732975    2.429641    0.065142
    11          6           0        2.853723    1.410599    0.042378
    12          6           0        2.170280    0.143012    0.031652
    13          6           0        2.479006   -2.461913    0.035256
    14          1           0        1.881198   -2.685498   -0.848948
    15          1           0        3.323672   -3.152922    0.046757
    16          1           0        1.860673   -2.681007    0.906300
    17          6           0        6.537567    0.400850    0.032818
    18          1           0        6.903668    0.464409   -0.998043
    19          1           0        6.892181    1.289562    0.559586
    20          1           0        6.996377   -0.478677    0.489225
    21          7           0       -0.107505   -1.267172   -0.000392
    22          6           0       -0.618816   -1.913510   -1.135067
    23          6           0       -0.650859   -1.920469    1.115188
    24          6           0       -1.524206   -2.934184   -0.746507
    25          6           0       -0.294214   -1.738489   -2.483786
    26          6           0       -1.544724   -2.938639    0.694700
    27          6           0       -2.145240   -3.729901   -1.712619
    28          6           0       -0.920972   -2.543752   -3.428397
    29          1           0        0.436549   -1.009368   -2.801041
    30          6           0       -2.192870   -3.740358    1.637766
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    31          6           0       -1.849259   -3.524917   -3.053527
    32          1           0       -2.841323   -4.506781   -1.415494
    33          1           0       -0.677097   -2.411637   -4.476605
    34          1           0       -2.880169   -4.515288    1.316113
    35          1           0       -2.322463   -4.135487   -3.813741
    36          6           0       -1.017736   -2.565304    3.395013
    37          1           0       -0.803568   -2.439935    4.450514
    38          6           0       -0.364539   -1.754131    2.473654
    39          1           0        0.356953   -1.027187    2.816148
    40          6           0       -1.935029   -3.543910    2.987796
    41          1           0       -2.429537   -4.159229    3.730415
    42          6           0       -0.418469    1.289455    0.002140
    43          6           0       -0.973755    1.777742    1.210684
    44          6           0       -0.936991    1.786015   -1.219329
    45          6           0       -0.357480    1.547627    2.481135
    46          6           0       -2.159960    2.601421    1.195039
    47          6           0       -2.123304    2.609612   -1.233869
    48          6           0       -0.282800    1.564309   -2.472229
    49          6           0       -0.888473    2.036296    3.642743
    50          1           0        0.585707    1.015385    2.511725
    51          6           0       -2.709107    3.057304    2.432932
    52          6           0       -2.730957    2.956652   -0.027130
    53          6           0       -2.635034    3.073814   -2.484653
    54          1           0        0.660833    1.032038   -2.477969
    55          6           0       -0.778683    2.060838   -3.645952
    56          6           0       -2.098260    2.782306    3.623083
    57          1           0       -0.383472    1.860500    4.585888
    58          1           0       -3.616916    3.651011    2.403657
    59          1           0       -3.637795    3.553348   -0.038816
    60          6           0       -1.988617    2.806801   -3.657702
    61          1           0       -3.543427    3.667322   -2.478707
    62          1           0       -0.245557    1.891299   -4.574660
    63          1           0       -2.519331    3.147049    4.553084
    64          1           0       -2.381583    3.177786   -4.597483
    65          5           0        0.618358    0.069217    0.013403
 ---------------------------------------------------------------------
```

```
Compound 1c TS3-2rf-CN-An
 Method: b3lyp/6-311g(d,p)
 SCF Done:  E(RB3LYP) =  -1430.58203331     A.U. after    1 cycles
 Lowest frequency =  -37.8568

 Zero-point correction=                           0.526557
(Hartree/Particle)
 Thermal correction to Energy=                    0.555831
 Thermal correction to Enthalpy=                  0.556776
 Thermal correction to Gibbs Free Energy=         0.466997
 Sum of electronic and zero-point Energies=          -1430.055476
 Sum of electronic and thermal Energies=             -1430.026202
 Sum of electronic and thermal Enthalpies=           -1430.025258
 Sum of electronic and thermal Free Energies=        -1430.115036

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -0.021035   -2.291883   -2.526402
```

2	1	0	-0.450754	-1.305610	-2.718327
3	1	0	1.029744	-2.261675	-2.822342
4	1	0	-0.528371	-2.998928	-3.188118
5	6	0	-0.714502	-2.304799	1.243213
6	6	0	-0.733079	-3.685999	1.456821
7	1	0	-0.988561	-4.053293	2.447275
8	6	0	-0.462118	-4.600725	0.444354
9	6	0	-0.224131	-4.087713	-0.828335
10	1	0	-0.078658	-4.773885	-1.658539
11	6	0	-0.189646	-2.715424	-1.081776
12	6	0	-0.385459	-1.784154	-0.032196
13	6	0	-1.112085	-1.435859	2.418639
14	1	0	-1.466334	-0.452603	2.107508
15	1	0	-1.923984	-1.910937	2.975313
16	1	0	-0.279419	-1.291816	3.111633
17	6	0	-0.442965	-6.086096	0.709159
18	1	0	0.566406	-6.423547	0.969472
19	1	0	-1.100191	-6.352599	1.540413
20	1	0	-0.758833	-6.653370	-0.169914
21	7	0	1.278705	0.226630	-0.090621
22	6	0	1.904112	0.464807	1.141696
23	6	0	2.299528	0.119687	-1.043283
24	6	0	3.313838	0.421897	0.990280
25	6	0	1.336640	0.802676	2.373755
26	6	0	3.568369	0.204530	-0.412002
27	6	0	4.146017	0.646591	2.090783
28	6	0	2.182854	1.026640	3.453644
29	1	0	0.268888	0.921586	2.486600
30	6	0	4.737377	0.153415	-1.176040
31	6	0	3.576705	0.935329	3.323363
32	1	0	5.224160	0.609686	1.978064
33	1	0	1.753065	1.293541	4.412849
34	1	0	5.707776	0.210311	-0.694900
35	1	0	4.209420	1.115094	4.184805
36	6	0	3.385615	0.035359	-3.179935
37	1	0	3.325540	0.003194	-4.262178
38	6	0	2.209355	0.078397	-2.438936
39	1	0	1.253248	0.105744	-2.942454
40	6	0	4.642293	0.053267	-2.557828
41	1	0	5.541107	0.017082	-3.162407
42	6	0	-1.298540	0.855243	-0.439818
43	6	0	-2.688789	0.462970	-0.407333
44	6	0	-1.016326	2.272530	-0.394911
45	6	0	-3.152487	-0.850187	-0.720322
46	6	0	-3.713862	1.422494	-0.071533
47	6	0	-2.058006	3.210828	-0.043118
48	6	0	0.249373	2.852112	-0.715858
49	6	0	-4.480040	-1.189998	-0.657521
50	1	0	-2.446665	-1.598611	-1.035671
51	6	0	-5.083501	1.029105	0.016786
52	6	0	-3.358028	2.750965	0.151985
53	6	0	-1.777155	4.606059	0.077400
54	1	0	1.046227	2.225957	-1.074413
55	6	0	0.476827	4.201561	-0.625582
56	6	0	-5.465100	-0.250661	-0.264425
57	1	0	-4.779891	-2.197756	-0.922894
58	1	0	-5.815592	1.780617	0.292963
59	1	0	-4.128546	3.460372	0.440339

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    60          6           0       -0.534655    5.096935   -0.198045
    61          1           0       -2.585767    5.267488    0.370058
    62          1           0        1.451969    4.589581   -0.897895
    63          1           0       -6.506697   -0.544779   -0.208433
    64          1           0       -0.325196    6.157170   -0.117340
    65          5           0       -0.173874   -0.208762   -0.253440
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