Alma Mater Studiorum - Università di Bologna

SCUOLA DI SCIENZE

Dipartimento di Chimica Industriale "Toso Montanari"

Corso di Laurea Magistrale in

Chimica Industriale

Curriculum: Advanced Spectroscopy in Chemistry

Classe LM-71 - Scienze e Tecnologie della Chimica Industriale

Synthesis, characterization and DFT study of new azaborinine compounds

Tesi di laurea sperimentale

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Anno Accademico 2019-2020

ABSTRACT

In the framework of this thesis, a wide-ranging study of azaborinine derivatives was conducted, with a particular interest towards 9,10-B,N-phenanthrenes, holding an isosteric B-N unit in the place of a C=C bond and incorporating a B-C chiral axis. For this purpose, a preliminary theoretical study for four compounds of this class was carried out: conformational analysis and rotational energy barriers, UV-Vis absorption and fluorescence emission as well as theoretical ECD spectra of the atropisomeric structures were calculated by means of DFT and TD-DFT. An experimental attempt to synthesize and characterize another derivative of this class followed. The main synthetic concept evolved around the obtention of anti-aromatic 9-borafluorene precursors by boron-tin exchange from the reaction of a 9-stannafluorene derivative with boron reagents, followed by an aromaticity-driven ring-opening reaction of these borafluorene precursors with an organic azide. Several approaches based on similar previous works were reproduced to the closest possible version, as no absolutely inert conditions could be achieved, but the expected products were not formed; in one case, an open structure was obtained instead, for the formation of which a mechanism was proposed.

This thesis is dedicated to all my friends whom I hold very close to my heart.

To Bia, Milena, Diego, Dani and of course, my precious Adam.

For they have taught me that whatever we do is pointless, unless we do it with the people we love.

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1 Introduction

1.1 Azaborinines: a compound class of interest

Boron doping has attracted a lot of interest due to the electron-deficient nature of the sp^2-hybridized boron atom. Its empty *p* orbital acts as an excellent receptor of an electron pair, therefore boron-containing compounds, such as organoboranes, are classified as Lewis acids. This property finds application in fluoride anion sensing[1], as F^- act as Lewis bases, to afford fluoborate anions. Since organoboranes are air- and moisture-sensitive, more stable alternative structures are employed, such as systems where the B-C unit is replaced by a B-N moiety.

The replacement of carbon by a nitrogen atom is not random. In fact, the boron-nitrogen (B-N) moiety is an isostere of the C=C bond and can substitute the latter in aromatic systems[2], such as benzene, naphthalene and phenanthrene to afford (polycyclic) aromatic BN-heterocycles. The actual interest towards the incorporation of a B-N unit[3] emerges from the inherent polarity of the B-N bond, which can be employed to tune the physical, chemical and optoelectronic properties both in a molecular level and in solid state, by modifying the character of the frontier molecular orbitals[4].

Indeed, many BN derivatives, apart from being highly stable and good Lewis acids on the boron center, they also exhibit interesting optical properties, such as luminescence[1]: carbon's replacement by boron decreases the HOMO-LUMO gap, turning chemiluminescence more probable[3].

Overall, BN compounds possess fascinating features, which manifest themselves through a large scope of applications from materials science as optoelectronic materials, such as Organic Light-Emitting Diodes (OLEDs) and Organic Field-Effect Transistors (OFETs), to transition-metal catalysis to biochemistry and pharmacology, as potential new drug candidates[3].

BN-isosteres of Polycyclic Aromatic Hydrocarbons (PAHs) were first synthesized by Dewar and his team in the late 1950s[5]. In particular, their efforts were focused on the synthesis of polycyclic derivatives of 1,2-dihydro-1,2-azaborinine, such as BN-naphthalenes, BN- phenanthrenes[6] and B,N-tetraphenes.

(a) (b)

Figure 1 (a) The forefather 1,2-dihydro-1,2-azaborinine is an isostere of benzene (b) General structure of 9,10-B,N-phenanthrenes

In the framework of this thesis, special attention was drawn to 9,10-B,N-phenanthrene (BNP)-based derivatives, with different substituents at the boron and nitrogen centers, along with a particular interest to introduce a boron-carbon chiral axis for the generation of possible atropisomers.

1.1.1 Previous syntheses of 9,10-B,N-phenanthrenes

9,10-BNP compounds can be obtained through an aromaticity-driven ring-opening reaction of highly anti-aromatic boroles with azides[7]. These anti-aromatic 9-borafluorene precursors can in turn be obtained by boron-tin exchange from the reaction of 9-stannafluorene derivatives with a boron reagent. The reasoning behind the initial formation of a 9-stannafluorene derivative is the fact that this compound is air-stable and isolable, whereas a direct synthesis of the 9-chloro-9-borafluorene would be more trivial due to its moisture-sensitive nature[8] (it decomposes rapidly at ambient conditions) and to the many possible outcomes, depending on the success of the very sensitive lithiation process and the by-products that might form even when lithiation works successfully. Bulky substituents on the boron center and electronic stabilizing substituents can turn the otherwise unstable borafluorenes into air-stable compounds[8].

Mechanism of the ring expansion

Electronic and steric effects are the two key factors that govern the mechanistic pattern that the ring-expansion reaction will follow[9]. The electronic effect introduced by different substituents in the boron and nitrogen centers of the initial boroles and azides respectively affect only the reaction times (electron-withdrawing groups in both centers accelerate the reaction), but not the outcome of the reaction. Initially, an adduct forms between the azide – with different possible coordination modes – and the boron atom of the borole (Lewis acid-base adduct formation), followed by a re-arrangement into a fused bicyclic system and finally conversion either to the kinetic eight-membered heterocycle or to the thermodynamic 1,2-azaborinine, by N_2 expulsion[10]. Diels-Alder and nitrene insertion into the endocyclic B-C bond are not favored.

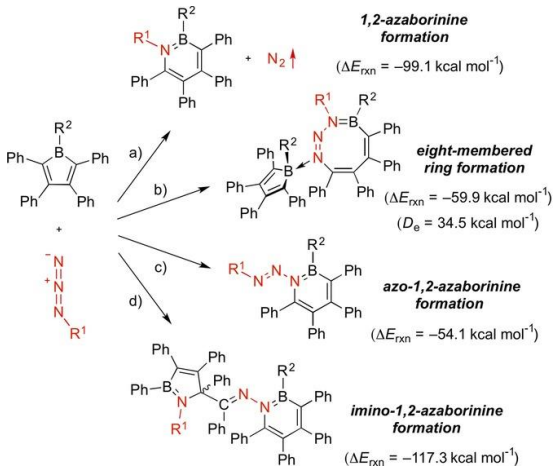
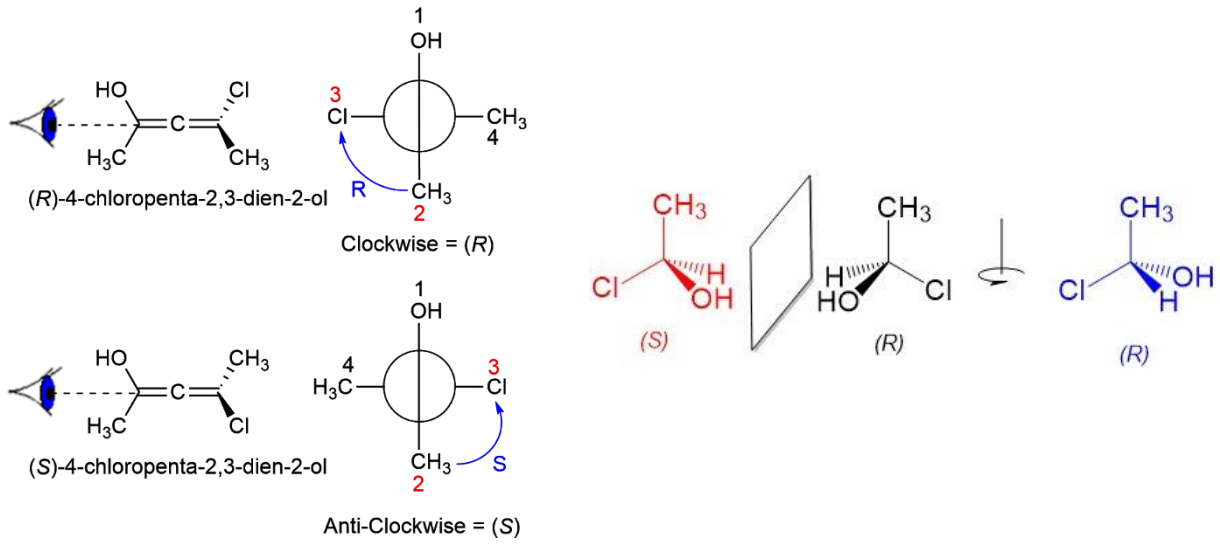


Figure 2 Possible routes for the reaction of a borole with an azide[9]

1.2 Chirality & atropisomerism: an interesting feature in azaborinine chemistry

Chirality[11] is a property whose presence in nature spans from elementary particles (e.g. helical neutrino) to entire organisms (such as bacteria, plants and sea shells). At the molecular level, chirality is a property of outstanding importance, as many biologically active compounds including pharmaceuticals, agrochemicals, nutrients etc. are chiral. A molecule is said to be chiral when it is not superimposable with its mirror image and constitutes with it an enantiomeric pair. The two enantiomers exhibit different chemical, physical and biological properties in a chiral environment, such as the human body, therefore the need for enantiomerically pure compounds (e.g. in drug design) has propelled the search for synthetic and analytical ways for their synthesis, separation and characterization. An interesting property of chiral molecules is that they exhibit optical activity; as an example, they rotate to the same extent (angle of optical rotation) but in opposite ways the polarization plane of plane-polarized light.

Axial chirality is a peculiar form of chirality, in which the chiral property emerges from the presence of a chiral axis and not from – the most familiar case of - a stereogenic center.



(a) (b)

Figure 3 (a) Axial chirality along the C=C=C axis (b) Chirality due to a stereogenic carbon atom

Atropisomerism (often interchangeably termed "axial chirality") is a special case of axial chirality and results from the hindered rotation about a single bond. Since no bond cleavage/formation is involved, racemization occurs "spontaneously" *via* bond rotation, making atropisomerism a dynamic form of axial chirality[12]. Due to atropisomerism, several conformers that can be isolated as distinct stereoisomers at a given temperature are generated, as the rotational energy barrier for their interconversion is very high. Atropisomers - a term originally coined by R. Kuhn[13] in 1933 – are

exactly these stereoisomers (enantiomers or diastereomers) that emerge from the hindered rotation about a single bond. The term originally referred to biaryl systems, but has since extended to include many more.

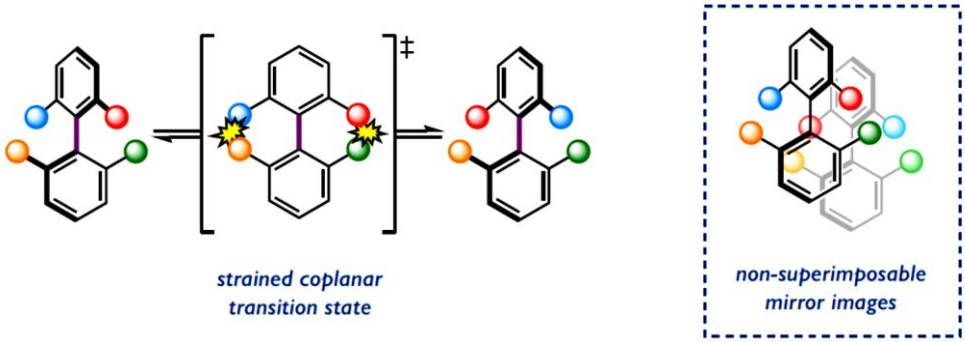


Figure 4 Axial chirality and atropisomerism in biaryls

In order for atropisomers to be distinguishable and separable at a given temperature, a half-life of 1000s (16.7 min) is arbitrarily set as the lower limit. At room temperature (25°C), this half-life is achieved by a rotational energy barrier of at least 24 kcal/mol[4].

This stereodynamic process can be monitored by means of kinetic studies (i.e. thermal racemization with chiral HPLC) or dynamic studies (i.e. dynamic NMR or dynamic enantioselective HPLC). For dynamic NMR, a chirality probe within the molecular scaffold is necessary for the recognition of atropisomerism.

The rotational stability of axially chiral biaryl compounds is determined by three major factors[14], namely the combined steric hindrance introduced by the substituents that are close to the chiral axis, the presence of bridges and the possible involvement of other means of rotation apart from the physical (thermal) rotation, such as photochemically or chemically induced rotations. Additionally, electronic effects and the bond length of the atoms that form the chiral axis also play an important role in the stability of the atropisomers.

In the case of substituted azaborinines with a boron-carbon stereogenic axis, the B-C_{sp^2} bond length, being longer than the C_{sp^2}-C_{sp^2}, lowers the energy barrier for the bond rotation, decreasing its thermal stability by about 12-13 kcal/mol with respect to the carbon analogues.

There are two systems for the nomenclature of axially chiral molecules (Figure 5). The R_a/S_a - where the subscript "*a*" stands for axial chirality – is based on a Newman projection along the chiral axis. The four groups that constitute the projection are ranked according to the Cahn–Ingold–Prelog (CIP) priority rules and the highest-priority group is placed closer to the observer, so that a clockwise rotation from the highest (1) to the lowest (4) priority group gives the R_a stereoisomer, while an anti-clockwise rotation gives the S_a stereoisomer. The *P*/*M* approach takes into consideration the dihedral angle that is formed around the chiral axis, by the A,B,C and D atoms, where B-C corresponds to the

chiral axis and A and D are the atoms with the highest CIP priority that are attached to B and C respectively. Atom A is placed closer to the observer and depending on the direction of the rotation from A to D, the isomers are named *P* for a clockwise rotation and *M* for an anti-clockwise rotation.

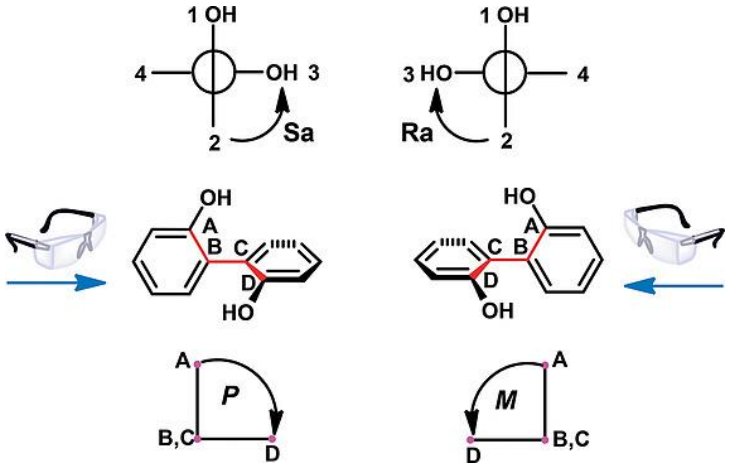


Figure 5 The R_a/S_a (up) and P/M (bottom) approaches for the nomenclature of stereogenic axes

1.3 Electronic Circular Dichroism (ECD)

ECD spectroscopy[15] is the chiroptical equivalent of UV-Vis spectroscopy and belongs to the arsenal of techniques employed for the study of chirality and the assignment of absolute configuration. It is based on the differential absorption $\Delta A(\lambda)$ of right-handed (clockwise, R-CPL) and left-handed (anti-clockwise, L-CPL) circularly polarized light (light in which the electric and magnetic fields rotate around the direction of propagation while remaining perpendicular to it and to each other) by chiral molecules:

$$\Delta A(\lambda) = A_r(\lambda) - A_l(\lambda) = [\varepsilon_r(\lambda) - \varepsilon_l(\lambda)] \cdot l \cdot c = \Delta E(\lambda) \cdot l \cdot c$$

ΔE: $L \cdot mol^{-1} \cdot cm^{-1}$

ECD spectra are plots of ellipticity (θ) *versus* wavelength (λ)[16]. Ellipticity is the result of the distortion of circularly polarized light in response to its differential absorption and is related to ΔE as following:

$$\theta = 3298.2 \cdot \Delta E$$

θ: $deg \cdot cm^2 \cdot dmol^{-1}$

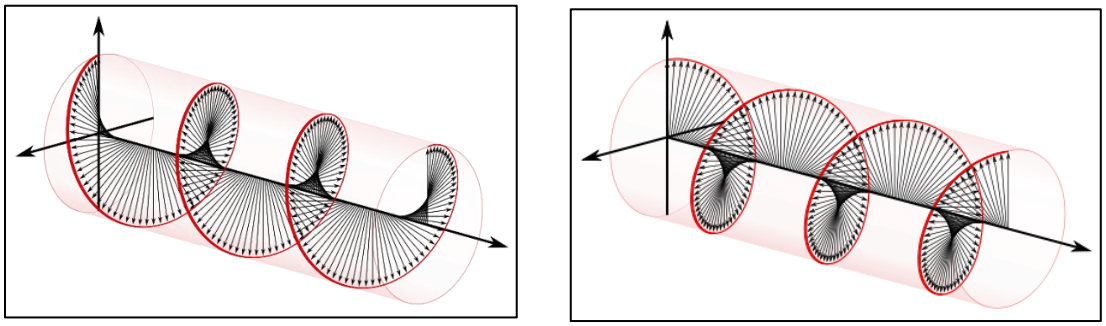


Figure 6 R-CPL and L-CPL, as defined from the point of view of the receiver

In general, enantiomers or even different conformations of the same absolute configuration give rise to bands of the same amplitude but of opposite sign in an ECD spectrum[17]; this is the so-called "Cotton effect" or "dichroic peak". Cotton effect is considered to be positive when the sign of the dichroic band is first positive and then negative with decreasing wavelengths. In the reversed case, it is considered to be negative.

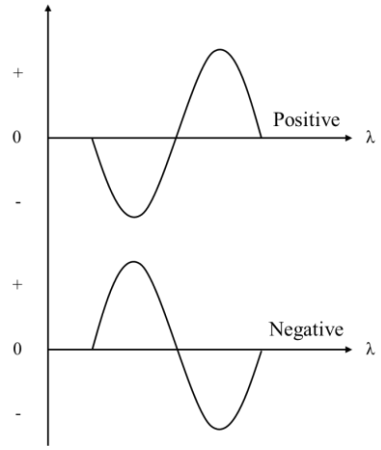


Figure 7 Positive (top) and negative (bottom) Cotton effect

Absorption of UV-Vis radiation is oftentimes associated with the presence of a chromophore. In cases where more than one chromophores with strong electric-dipole allowed transitions are present in a single molecule, exciton coupling can be observed as a result of the coupling of chromophores that have strong electric-dipole allowed transitions. In exciton coupling, the delocalized excited states are split into two or more states. This process is described as "exciton splitting" (Figure 8). When the coupled chromophores are identical, the exciton splitting is symmetric, separated by the quantity $2V_{12}$, called "Davydov splitting".

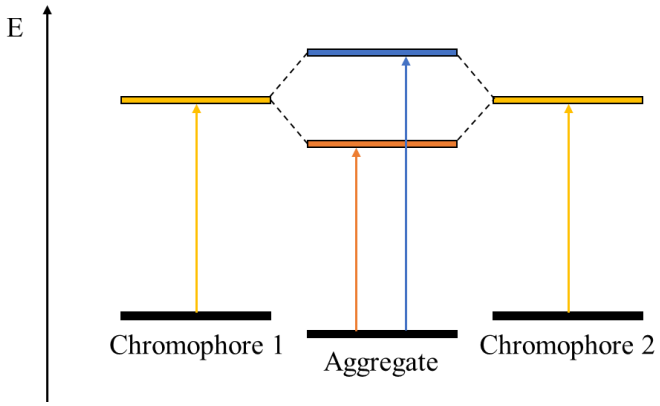


Figure 8 The exciton splitting for two identical, coupled chromophores

Excitation into these split states is perceived as a split or broadening of the UV-Vis absorption band. In ECD spectra, exciton coupling often results in a bisignate couplet, when the transition moments of the chromophores are not co-planar.

ECD spectra bear information about the absolute stereochemistry of a molecule, but it is rather trivial to assign the peak's sign to a specific enantiomeric structure or conformation and *vice-versa*: predicting the sign of the peak from the structure is a difficult task. Nevertheless, bands could potentially be assigned to specific enantiomers/conformations by comparison with experimental spectra of other, similar structures with a confirmed/known handedness/absolute configuration and/or conformation or with theoretically derived spectra.

Time-dependent density functional theory (TD-DFT) with range-separated hybrid functionals, such as CAM-B3LYP and ωB97X-D, gives accurate predictions of various chiroptical properties with a reasonable computational cost[18]. ECD spectra in particular are derived by prediction of the rotational strength. In general, functionals affect the quality of the theoretically predicted spectra a lot more than basis sets do. An effective combination of functional/basis set can only be established through a trial-and-error approach and might differ from one case to another. Typically, a molecule's environment - the presence and nature of a solvent being a simple example – can greatly impact the resulting ECD spectrum, therefore it is common to include a solvation model in its theoretical calculation, so that it matches as much as possible the experimental one.

1.4 Fluorescence[15,19]

Fluorescence - along with phosphorescence - is a luminescence property which involves the fast (within a few nanoseconds) de-excitation of an electronically excited state through emission of a photon, when the electronic transition occurs between two states of the same multiplicity (e.g. singlet excited state – singlet ground state). Since a fraction of the energy absorbed during photon absorption is dissipated into the surroundings through radiationless decay and thermal equilibration, the energy of the emitted photon is usually lower than that of the absorbed photon. The consequent shift of the emission maximum with respect to the absorption maximum in the absorption/emission spectrum, is referred to as Stokes shift and is attributed to the vibrational relaxation (internal conversion, no spin-change) occurring after the initial photon absorption and within the same electronically excited state. Generally, structural rigidity can act as an inhibiting factor for vibrational (non-radiative) decay to occur. A schematic representation of these processes is depicted in Figure 9.

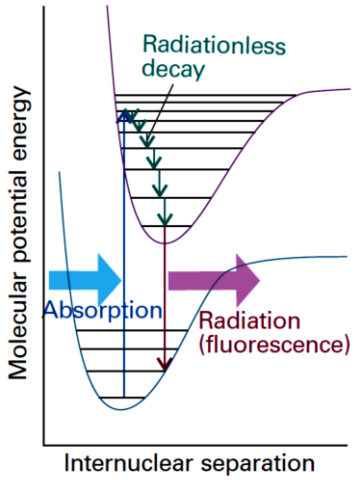


Figure 9 The steps leading to fluorescence[15]

In the context of fluorescence spectroscopy, quantum yield (Φ) is defined as the ratio of the photons emitted over the photons absorbed and serves as an indication of the intensity of the fluorescence phenomenon.

1.4 Computational studies

1.4.1 Density Functional Theory (DFT)[20,21]

Density Functional Theory (DFT) is a computational method, result of the work of Hohenberg, Kohn and Sham, which calculates the electron density and from that derives the Hamiltonian for the energy, which is a "Functional" of that density, the minimization of which reveals the ground state energy of a system from which all other related properties can be deduced, clearly working its way around the many-electron wavefunction approximations, such as the Hartree–Fock (HF) for the elucidation of the electronic structure of a system.

Coulomb, exchange and correlation interactions govern the electron motion. Exchange interaction is directly linked to the Pauli exclusion principle (fermionic wavefunctions should be anti-symmetric), whereas correlation energy is a measure of the total influence and is often considered as the difference between the exact energy and the HF energy (with an infinite basis set been used) of a system. DFT method is taking into consideration the exchange-correlation energy in contrary to other, older wave-function established methods/approaches, such as the HF, which only considers the exchange (through the incorporation of Slater Determinants). Exchange and correlation interactions are derived by various approximations, the so-called Exchange-Correlation Functionals (XCF). Since in most cases the atomic and molecular systems are inhomogeneous in terms of the spatial electron density, the uniform electron gas approach as seen by the Local Density Approximation (LDA) XCF is not a sufficient model. In this regard, density gradient corrections present in the Generalized-Gradient

Approximation (GGA) and the meta-GGA give a better insight of inhomogeneous systems. A representation of the different approximations available is summarized in the so-called Jacob's ladder. Moving upwards the ladder of DFT provides in general more accurate approximations until the ideal of the exact energy of a system is reached (Figure 10).

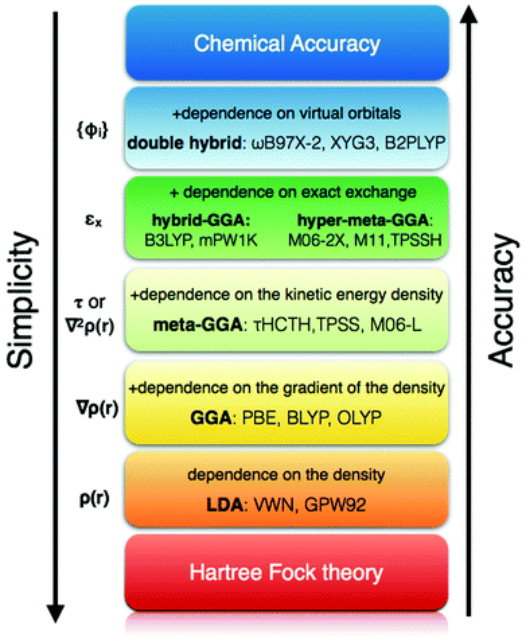


Figure 10 Jacob's ladder for DFT calculations[22]

Overall, DFT is established as an efficient method for the simulation of the electronic structure in terms of both computational cost and accuracy provided.

TD-DFT is an extension of the "static" DFT (in which no perturbation occurs), that is applied for the treatment of time-dependent phenomena, such as electronic excitations. In this context, it is ideal for the calculation of excited-state properties, excitation energies and optical spectra (e.g. UV-Vis and ECD). The accuracy of a TD-DFT calculation largely depends on the XC functional and - to a lesser extent - on the basis set used.

In the study of organic compounds, B3LYP hybrid-GGA functional has emerged as a good compromise between computational cost and accuracy[23] and it is by far the most commonly used in gas-phase calculations, while CAM-B3LYP is shown to afford very accurate results in the study of excited states.

Pople split-valence basis sets are the most common in computational organic chemistry and particularly in conformational analysis with 6-31G(d) being the smallest one and the one that is usually employed in geometry optimizations, as it provides a good performance/computational time ratio. It includes polarization functions (d functions on heavy atoms), but no diffuse functions.

2 Aim of the Thesis

This thesis was a theoretical and experimental exploratory study of new BNP derivatives. Theoretical DFT calculations were performed for the four compounds depicted in Figure 11 for the validation of their atropisomeric nature and the investigation of all the possible ground-state conformations and their relative populations. Moreover, a TD-DFT calculation was carried out for the prediction of the ECD spectra for the *P* and *M* atropisomers of compounds **2** and **3** respectively, in order to be used as a reference for the assignment of the correct atropisomer in experimental spectra. Lastly, a 7-step calculation cycle was performed for the study of UV-Vis absorption and fluorescence emission as well as for the evaluation of the solvatochromic effect generated by the solvent shift from the apolar *n*-hexane to THF and to the most polar ACN.

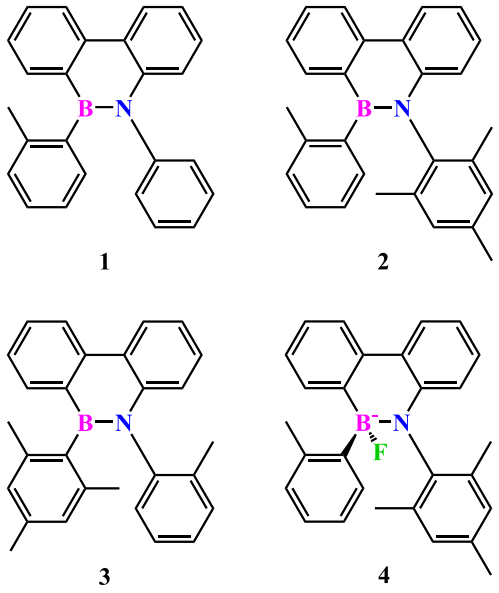


Figure 11 The four computationally studied compounds

In the experimental part, the synthesis and spectroscopic characterization of a compound similar to the ones theoretically calculated was attempted. For this purpose, the efficiency of several previously developed synthetic procedures was tested for the synthesis of compound **10**. The synthetic scheme involved a boron-tin exchange between a 9-stannafluorene derivative and boron reagents towards 9-borafluorene precursors, followed by a ring-opening reaction of the latter with an organic azide.

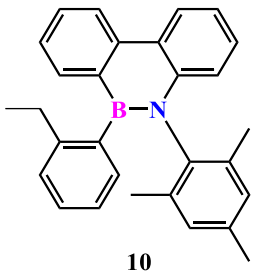


Figure 12 The experimentally attempted compound

3 Results and Discussion

3.1 DFT & TD-DFT calculations

All calculations were performed with the Gaussian 16 computational chemistry software.

3.1.1 Ground and transition state optimization – Vibrational frequency calculation

The ground state calculations were performed both in the gas phase and in acetonitrile (ACN) as a solvent, while the transition states were calculated only in the gas phase. For comparison purposes, all the data presented here for the ground states refer to the gas phase calculations. Both ground and transition states were calculated at the B3LYP/6-31G(d) level of theory.

As a starting point, conformational stability at room temperature was investigated and the rotational energy barrier for the interconversion between the *P* and *M* enantiomeric atropisomers was found in three out of the four cases greater than 25 kcal/mol. This energy barrier is expressed as the relative energy between the transition state and lowest-energy ground state absolute energies. Ground-state conformational search and optimization (in which only one enantiomer was taken into consideration) as well as transition-state optimization followed.

Vibrational analysis of the optimized structures provided evidence that the ground and transition states found were correct: ground states only had real/positive frequencies, whereas transition states had a single imaginary/negative frequency (a negative/imaginary frequency corresponding to a saddle point indicates the presence of a transition state).

The population of the different possible ground states found for each compound was determined with the Boltzmann distribution, based on the relative enthalpy of the found ground states, for a system in thermal equilibrium, at a fixed temperature T = 298 K.

All possible ground and transition states found for all four compounds computationally studied, along with the corresponding 3D structures, dihedral angles and absolute and relative energies are given in Tables 1-4.

Compound **1** has the simplest combination of substituents in the B- and N- positions. The energy barrier for the interconversion between the *P* and *M* enantiomer was found equal to 25.433 and 25.631 kcal/mol (the two values correspond to the two possible transition states TS1 and TS2, Figure 13), suggesting that the two atropisomers are distinguishable and separable at room temperature. Depending on the rotation of the *o*-tolyl substituent, two transition states emerge; the one in which the methyl group is rotated towards the phenyl substituent (TS2) is energetically higher, due to the steric hindrance generated. Therefore, it is assumed that TS1 is the preferred route for the *P*-*M* interconversion. Conformational search revealed the existence of only one conformation that can be

adopted by each enantiomer (*P* and *M*, Figure 13), in which both substituents lie almost perpendicular to the plane of B,N-phenanthrene (dihedral angle N1-B2-C22-C21 for the *o*-tolyl substituent).

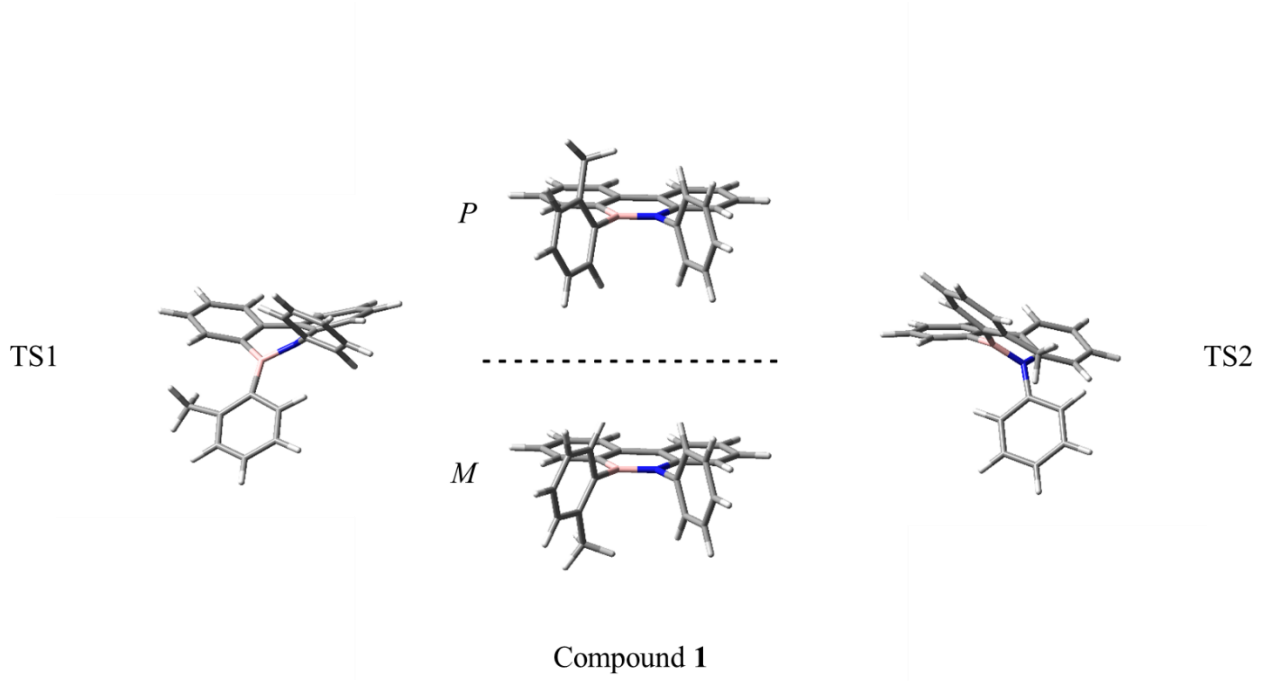
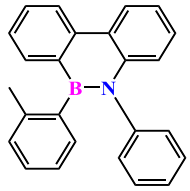
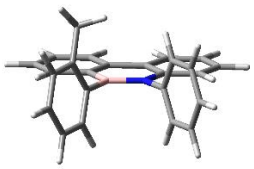
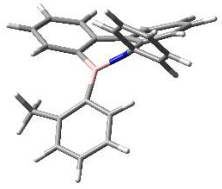
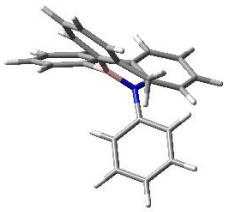


*Figure 13 The P and M enantiomers of compound **1** along with the two possible transition states for their interconversion*

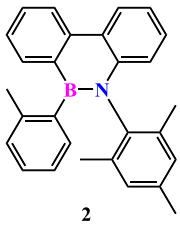
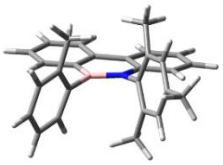
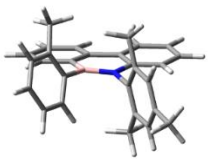
*Table 1 Ground state and transition states for compound **1***

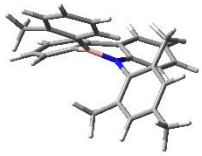
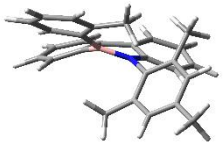
 1	**3D Structure (*P* enantiomer)**	**Dihedral Angle (°)**	**Total Energy (a.u.)**	**Relative Enthalpy (kcal/mol)**
GS		99	-1044.398	0.000
TS1		179	-1044.357	25.433

TS2		-1	-1044.356	25.631

In compound **2**, the phenyl group on the nitrogen atom of compound **1** is replaced by the more sterically hindered mesityl moiety. In this case, the *ortho syn* methyl group of the mesityl moiety skews out of perpendicularity the *o*-tolyl substituent, giving rise to two possible ground states. Indeed, for each enantiomer two ground state conformations were found, GS1 and GS2 (Table 2), populated 16.2% and 83.8% respectively in ACN and at room temperature, with a relative energy of less than 2 kcal/mol. The major difference observed between these two ground states is the orientation of the methyl group of the *o*-tolyl substituent, expressed through the value of the N1-B2-C22-C21 dihedral angle; in GS1 it points "inwards", while in GS2 it points "outwards". As far as the transition states are concerned, TS1, being energetically lower than TS2, is considered to be the favored transition state for the atropisomeric interconversion. The steric hindrance introduced by the mesityl substituent is portrayed by an increase of the energy barrier by 1.7 kcal/mol for the interconversion of the atropisomeric pair, with respect to compound **1**.

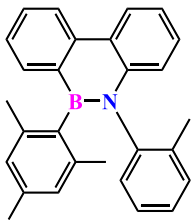
*Table 2 Ground states and transition states for compound **2***

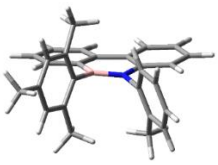
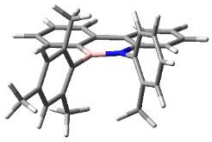
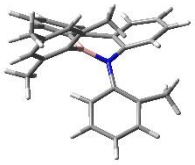
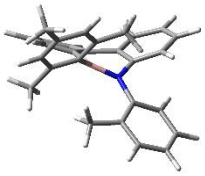
 2	**3D Structure (*P* enantiomer)**	**Dihedral Angle (°)**	**Total Energy (a.u.)**	**Relative Enthalpy (kcal/mol)**
GS1		85	-1162.347	0.900
GS2		114	-1162.349	0.000

TS1		-174	-1162.305	27.146
TS2		10	-1162.301	29.546

Compound **3** has the same substituents as **2**, but interchanged between the boron and nitrogen centers. In this particular case, the chiral axis is located along the N-$C_{o\text{-tolyl}}$ bond and the dihedral angle is defined as C20-N1-C24-C50. Again, the thermal stability of the *P* and *M* enantiomers was confirmed by the high rotational energy barrier, as indicated by the relative energy of the two possible transition states (~35 kcal/mol). This energy barrier is much higher than that of compound **2**, because the N-*o*-tolyl bond is shorter than the B-*o*-tolyl, creating a greater steric hindrance close to the phenanthrene scaffold. For each atropisomer, two ground states were found (GS1 and GS2, Table 3), with a relative energy of less than 2 kcal/mol; GS1 was 89% and GS2 was 11% populated in ACN, at room temperature. Again, the difference observed between the two ground states is the orientation of the methyl group of the *o*-tolyl substituent; in GS1 it points "outwards", while in GS2 it points "inwards". Despite the fact that the two transition states are energetically very close, TS1 is slightly more stable (as seen from the relative enthalpy values) and is thus expected to be more probable than TS2.

*Table 3 Ground states and transition states for compound **3***

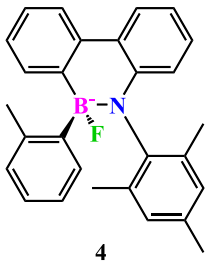
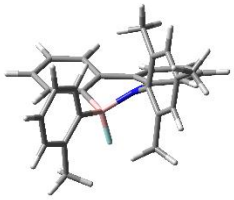
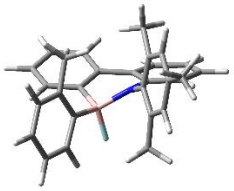
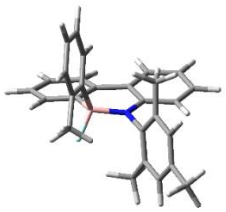
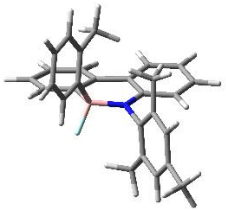
 3	**3D Structure (*M* enantiomer)**	**Dihedral Angle (°)**	**Total Energy (a.u.)**	**Relative Enthalpy (kcal/mol)**

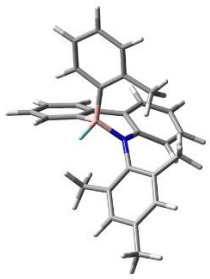
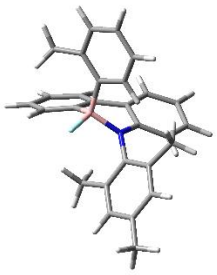
GS1		-74	-1162.347	0.000
GS2		-95	-1162.345	1.290
TS1		23	-1162.290	35.178
TS2		-177	-1162.290	35.353

The distinct case of compound **4** stems from the tetrahedral nature of the boron atom. Based on the nomenclature of stereocenters, the isomer depicted hereafter (Table 4) is the *R*. This compound was studied since coordination with fluoride anions has shown to enhance fluorescence. Here, the conformational analysis suggested two ground states, GS1 and GS2 which differ in the extend of the torsion of the B-N bond (illustrated by the dihedral angle C20-N1-B2-C3). Each ground state can in turn adopt two different diastereotopic conformations; one in which the methyl group of the *o*-tolyl substituent points towards the F atom and one in which it points away from it, indicated as "0" and "180" respectively. The transition states concern two separate processes: the ring flip which converts GS1-0-R to GS2-0-R and GS1-180-R to GS2-180-R and the phenyl group rotation that turns GS1-0-R to GS1-180-R and GS2-0-R to GS2-180-R. In Table 4, only the transition states that concern the rotation of the phenyl group are reported, since the ring flip is expected to have a very small energy barrier and is not of interest for the study of atropisomerism. The dihedral angle used for the description of the transition sates is N1-B2-C22-C23. The energy barrier for the diastereotopic

interconversion is found to be 13.4 kcal/mol, meaning that the separation of the atropisomers is not possible at room temperature, but dynamic NMR could be employed for their study.

*Table 4 Ground states and transition states for compound **4***

 4	**3D Structure**	**Dihedral Angle (°)**	**Total Energy (a.u.)**	**Relative Enthalpy (kcal/mol)**
GS1-0-R		-48	-1262.271	1.696
GS1-180-R		-48	-1262.271	1.734
GS2-0-R		15	-1262.273	0.448
GS2-180-R		10	-1262.274	0.000

TS1-P-90		-29	-1262.242	19.639
TS1-M-90		155	-1262.252	13.448

3.1.2 ECD spectra simulation

In the calculation of the ECD spectra, 6-311++G(2d,p) was the basis set that was used with four different functionals: BH&HLYP, CAM-B3LYP, LC-wB97XD and M06-2x, in order to have data redundancy and enhanced reliability. The default SCRF method which applies the integral equation formalism (IEF) variant in the frame of the Polarizable Continuum Model (PCM) was applied, with ACN as solvent. For each simulation, excited states were set to 70 and the ECD spectra were obtained by applying Gaussian shapes (half-width at half height = 0.25 eV) in the range 160-400 nm. Nevertheless, due to ACN's UV-Vis absorbance cut-off wavelength at 190 nm, the wavelength axis was adjusted accordingly.

Since each enantiomer/conformer gives rise to a different - oftentimes of opposite sign - signal in the ECD spectrum, for each compound studied, all the possible ground state geometries were considered for a single atropisomer: their relative populations were taken into consideration and an average ECD signal was calculated. Spectral averaging in a weighed way is allowed since ECD spectroscopy is a "fast" spectroscopy, meaning that all conformations present will contribute independently to the observed experimental signal, according to their relative populations.

As more than one chromophores are present in the studied compounds, exciton coupling should be observed. In fact, complicated ECD spectra are expected: since the chromophores are not identical, their coupling is non-degenerate and the exciton splitting is not symmetric. Moreover, as the chromophores have a relative orientation other than co-planar, the magnetic moments generated by the oscillating dipoles will not be orthogonal, thus contributing to the appearance of bands of opposite sign.

Indeed, for compound **2**, for the *P* atropisomer, the ECD spectrum predicted by each functional is shown in Figure 14, where the contribution of each ground state is clearly illustrated as giving rise to bands of opposite sign. This finding suggests that the two ground-state conformations, having an adequately tilted *o*-tolyl group, adopt an overall opposite helicity, yielding opposite band signs. In addition, it implies that the final, weighed ECD spectrum should be very sensitive to the relative population of the two ground states making comparison to an experimental spectrum very challenging. In regard to the individual spectra generated for each ground state, the complexity of the total number of bands and their signs reflects the complexity of the chromophore coupling.

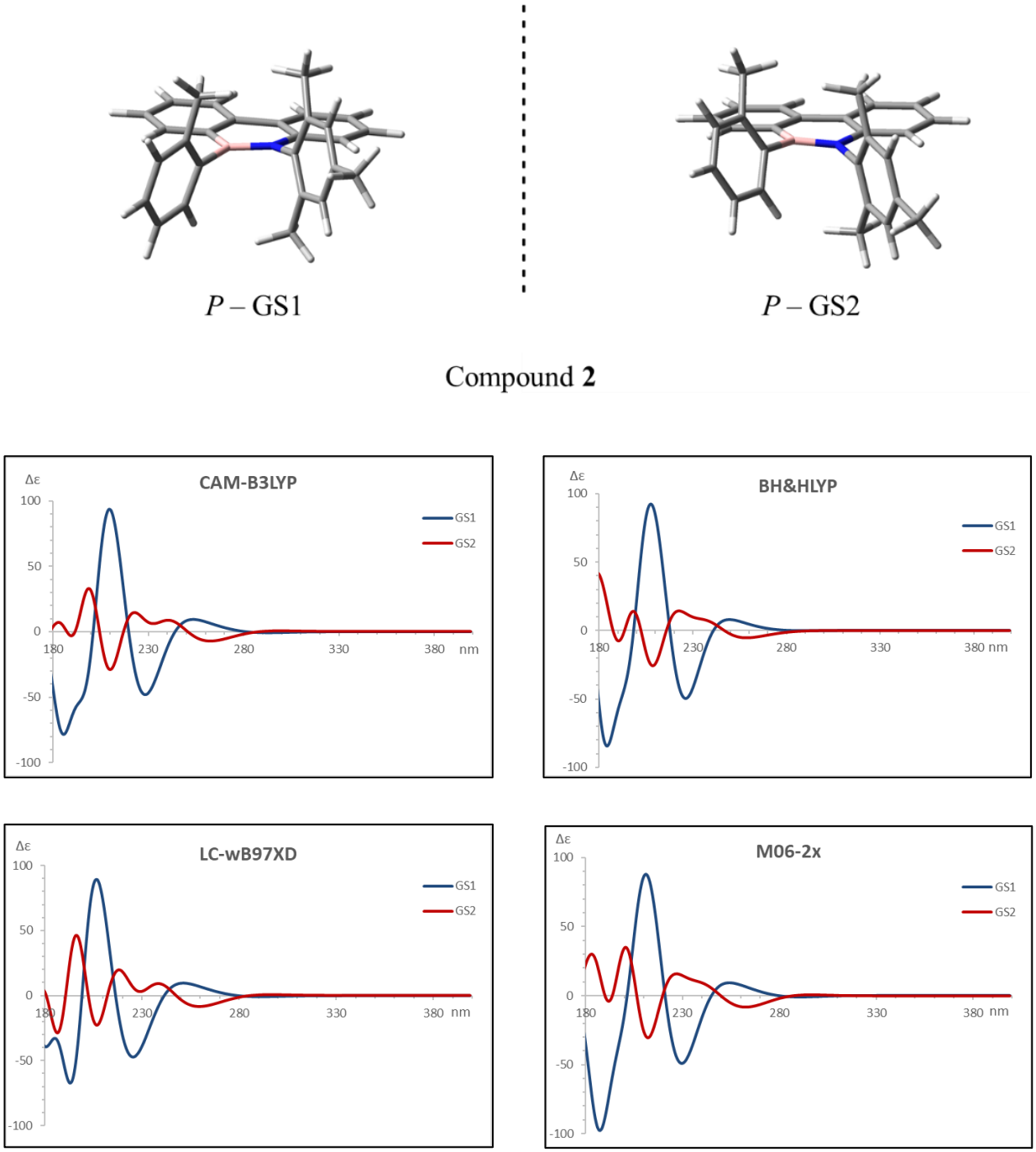


*Figure 14 Computed ECD spectra for the two ground-state conformations of the P atropisomer of compound **2***

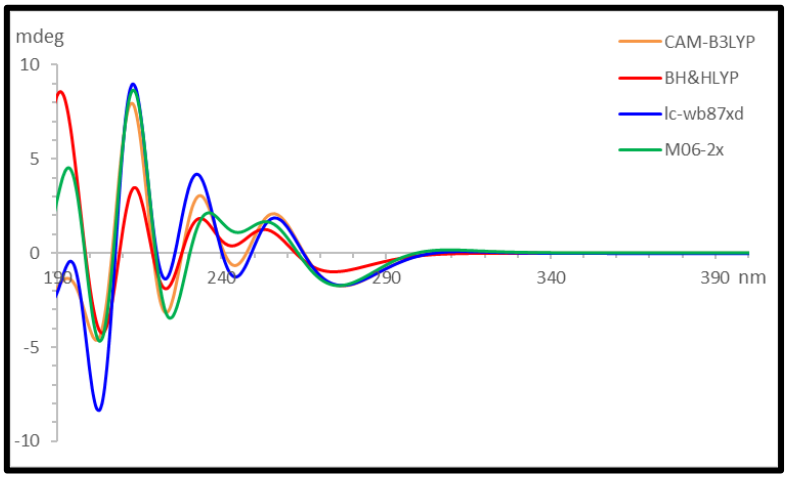
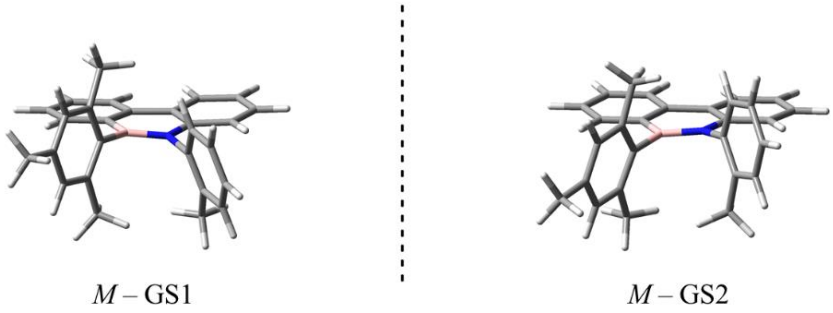


*Figure 15 The final, weighed theoretical ECD spectra of the P atropisomer of compound **2**, as computed by 4 different functionals*

In Figure 15 the final, conformationally averaged ECD spectrum is shown, in which the weighed by means of the Boltzmann distribution average of all populated ground-state conformations is depicted, as calculated by each functional. The four different functionals deliver spectra with the same general trend, proving the stability of the calculations.

For the *M* atropisomer of compound **3**, the simulated spectra for the two ground-state conformations calculated by each functional (Figure 16) exhibit similar shapes, with two negative bands at 200 and 230 nm and two positive bands at 215 and 245 nm. This similarity can be explained by the fact that the *o*-tolyl group, being close to perpendicularity in both conformations, affords similar helicity.



Compound **3**

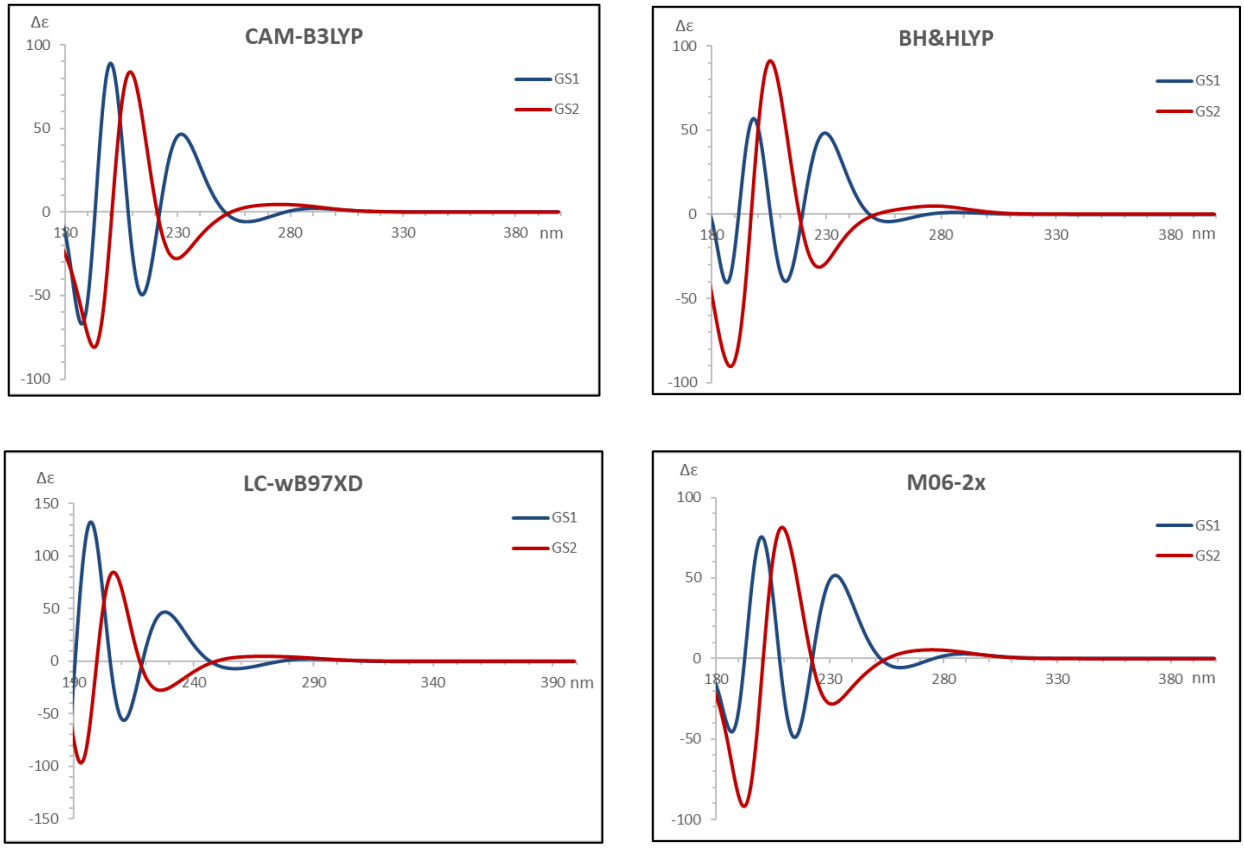


*Figure 16 Computed ECD spectra for the two ground-state conformations of the M atropisomer of compound **3***

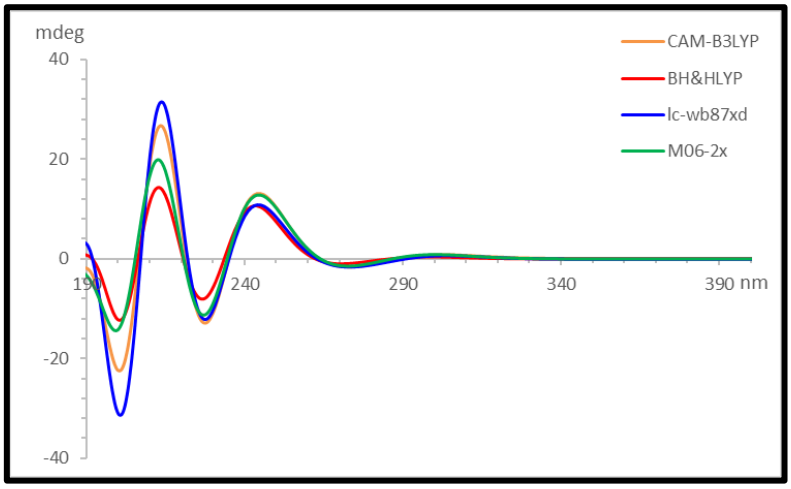


*Figure 17 The final, weighed theoretical ECD spectra of the M atropisomer of compound **3**, as computed by 4 different functionals*

The reliability of the simulated ECD spectra can only be confirmed by comparison with experimental spectra.

3.1.3 Fluorescence emission

For the calculation of the fluorescence emission, an optimized 7-step calculation cycle (Figure 18) was performed using the default SCRF method with three different solvents (*n*-hexane, THF and acetonitrile), including the following steps:

Step 1: Geometry optimization and vibrational frequency calculation for the ground state geometry, under "equilibrium solvation". For this step, CAM-B3LYP/6-31G(d) level of theory was employed, in order to reduce the computational time and cost for the geometry optimization. However, the basis set used in this step is not adequate for the calculation of the absorption energy in a later step.

Step 2: TD-DFT calculation of the vertical UV excitations towards the first three excited states, with a linear solvent response ("non-equilibrium solvation"). For this calculation, the same functional as in step 1 was used, with 6-31+G(d,p) as a basis set and the number of calculated excited states was set to 3, starting from the one of lowest energy. This step aims at predicting the transition with the highest oscillator strength (in all cases this was the transition towards the 1st excited state) and at defining its configuration (multiplicity and symmetry).

Step 3: Single-point calculation for the ground state energy with a larger basis set (6-31+G(d,p)). The solvation coordinates are saved to be used for the "non-equilibrium" energy calculation of the next step.

Step 4: TD-DFT calculation of the vertical excitation towards the 1st excited state (root=1) at the CAM-B3LYP/6-31+G(d,p) level, considering the calculated ground state energy and saved "non-equilibrium" solvent coordinates from step 3.

Step 5: TD-DFT geometry optimization of the excited state geometry (relaxation process) under "equilibrium solvation" at the same level of theory as in step 1.

Step 6: TD-DFT calculation of the vertical emission $S_1 \rightarrow S_0$*. The solvation coordinates are saved for the next step of "non-equilibrium solvation".

Step 7: The solvation coordinates saved in step 6 are used for the DFT single-point calculation of the ground state non-equilibrium energy, at the CAM-B3LYP/6-31+G(d,p) level of theory.

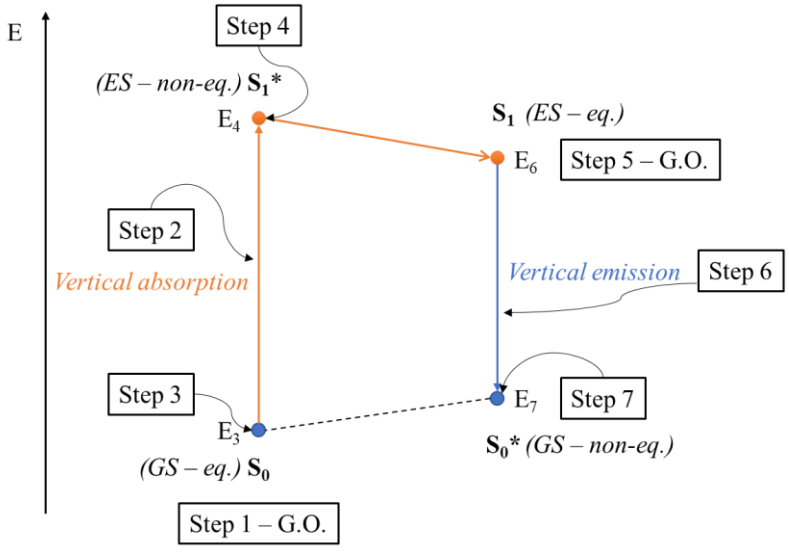


Figure 18 An illustration of the 7-step cycle

Geometry optimization in steps 1 and 5 is only performed in THF. These optimized geometries are then used directly for the calculations in *n*-hexane and acetonitrile, in order to reduce the computational time and cost.

The difference between the energy found at step 4 and the one calculated at step 3 is the vertical absorption energy ($E_4 – E_3$). The emitted radiation is the difference between the energy of step 6 and that of step 7 ($E_6 - E_7$) and is expressed in both terms of energy (eV) and wavelength (nm). The Stokes shift value is derived from the subtraction of the absorption wavelength from the emission wavelength ($\lambda_{emission} - \lambda_{absorption}$). All these data, for each compound studied, are reported in Tables 5, 6, 7 and 8.

For compound **1**, the orbital transition contributing with the highest probability to the excitation and emission to and from the first excited state is the MO (91) - MO (92), corresponding to the HOMO – LUMO (Figure 19).

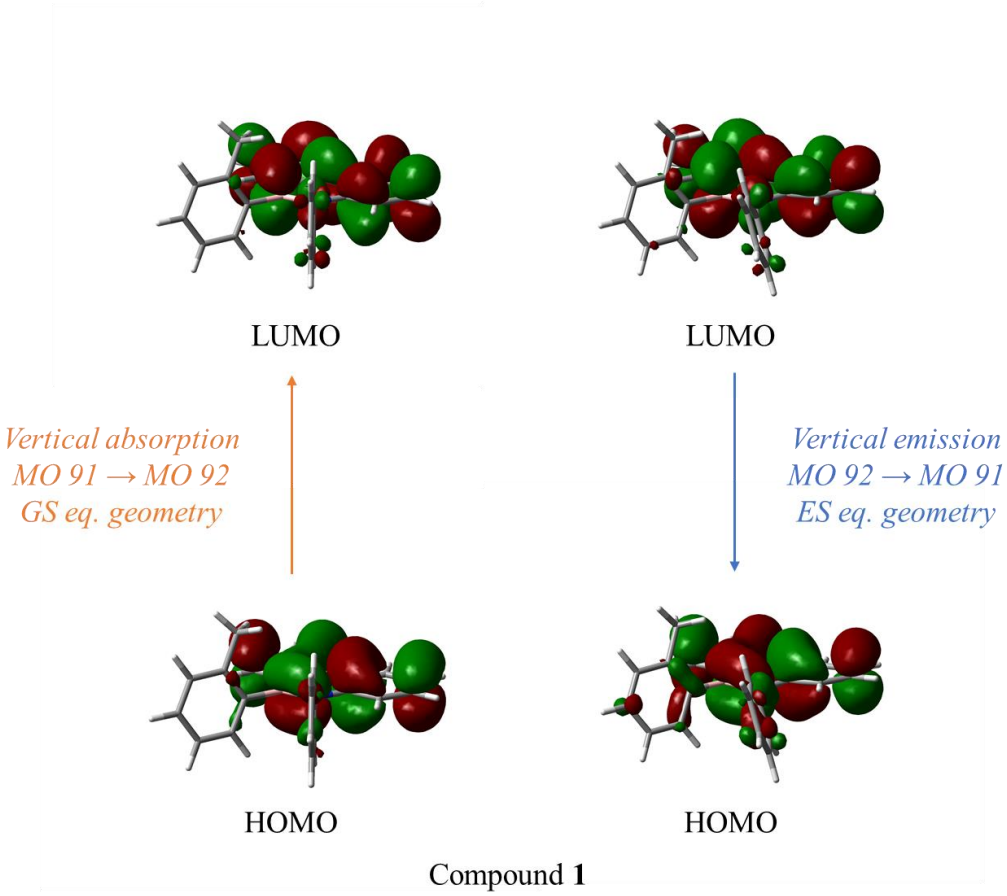


*Figure 19 Plots of the MOs contributing the most to the vertical absorption and emission related to the 1st excited state for compound **1** in THF*

Plotting of the molecular orbitals primarily involved in the electronic transition to the 1st excited state shows no interesting intramolecular charge transfer during excitation and emission, but reveals a structural change between the GS and ES geometries. To better portray this, the change of the dihedral angle C20-N1-C27-C26 is depicted in Figure 20.

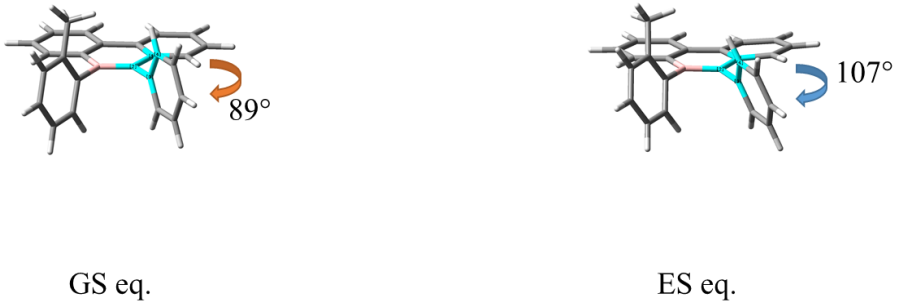


*Figure 20 GS_{eq} and ES_{eq} structures for compound **1** in THF*

This intramolecular relaxation process warns for possible accompanying electronic spatial re-arrangements. Indeed, an investigation of the MO (90) - MO (93) transition corresponding to the HOMO-1 – LUMO+1 and accounting as the second major contribution (7-9%) in the studied excitation shows that there is a minor charge transfer from the phenanthrene unit to the electron deficient boron center (Figure 21).

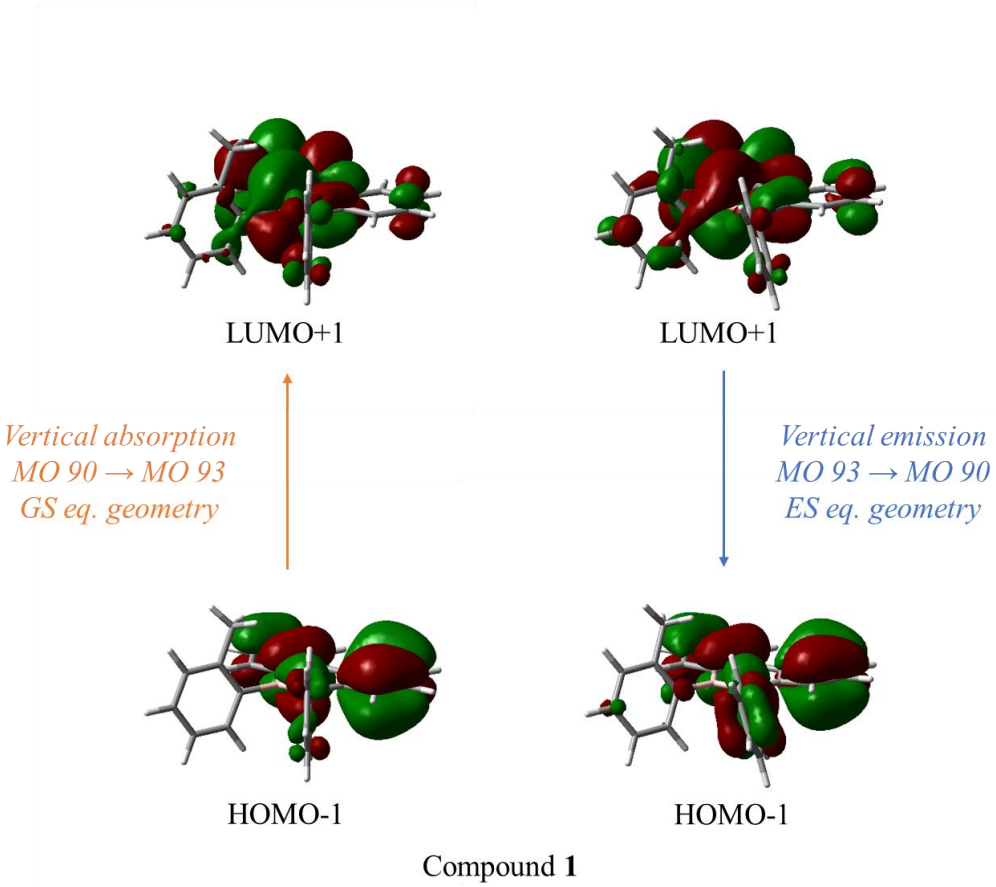
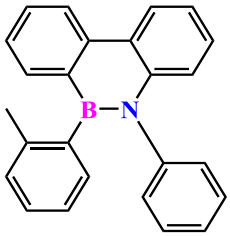


*Figure 21 The HOMO-1 - LUMO+1 transition for compound **1** in THF*

This stabilization through geometry optimization is expected to cause an increased Stokes shift, while the charge transfer is an indication that a solvatochromic effect might be observed. These speculations are confirmed by the results obtained (Table 5).

Table 5



1

Ground State	Solvent	$E_{absorption}$	$E_{emission}$	Stokes Shift
GS	*n*-hexane	4.498 eV	3.981 eV	35.796 nm
		275.647 nm	311.443 nm	
	THF	4.499 eV	3.966 eV	36.992 nm
		275.599 nm	312.591 nm	
	acetonitrile	4.501 eV	3.962 eV	37.476 nm
		275.473 nm	312.949 nm	

For compound **2**, for both ground-state conformations in all three solvents, the orbital transition contributing the most to the vertical absorption and emission towards and from the first excited state is the MO (103) – MO (104), which corresponds to the HOMO – LUMO transition (Figure 22).

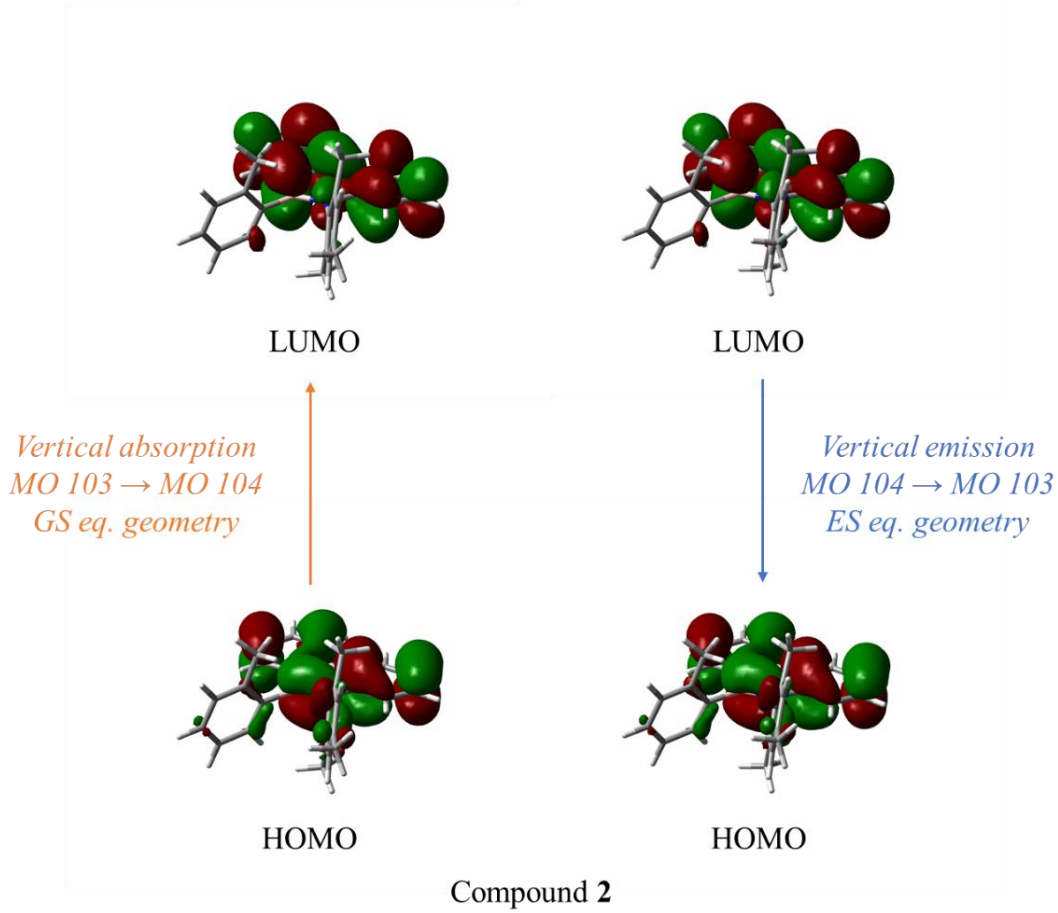
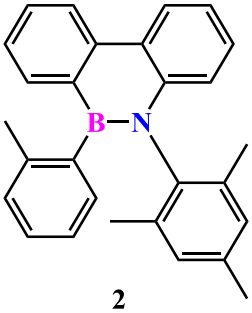


*Figure 22 Plots of the MOs contributing the most to the vertical absorption and emission related to the 1st excited state for GS1 conformation of compound **2** in THF*

As can be observed from Figure 22, the substituents of boron and nitrogen in both GS and ES structures have the exact same orientation, meaning that no intramolecular geometric relaxation occurred (hence small Stokes shift should be expected, Table 6), while the spatial electron density is confined mostly to the phenanthrene unit, implying that there is probably not a distinct electron donor-acceptor pair in the studied molecule to induce an intramolecular charge transfer during excitation.

Table 6



2

Ground State	Solvent	$E_{absorption}$	$E_{emission}$	Stokes Shift
GS1	*n*-hexane	4.476 eV	3.400 eV	32.960 nm
		277.002 nm	309.961 nm	
	THF	4.479 eV	3.974 eV	35.210 nm
		276.805 nm	312.015 nm	
	acetonitrile	4.483 eV	3.964 eV	36.193 nm
		276.581 nm	312.775 nm	
GS2	*n*-hexane	4.467 eV	3.987 eV	33.400 nm
		277.567 nm	310.967 nm	
	THF	4.469 eV	3.961 eV	35.617 nm
		277.419 nm	313.036 nm	
	acetonitrile	4.473 eV	3.949 eV	36.729 nm
		277.212 nm	313.941 nm	

For compound **3**, for both ground states and in all three solvents, the major orbital transition composing the excitation and emission to and from the first excited state is the MO (103) - MO (104), corresponding to the HOMO – LUMO (Figure 23).

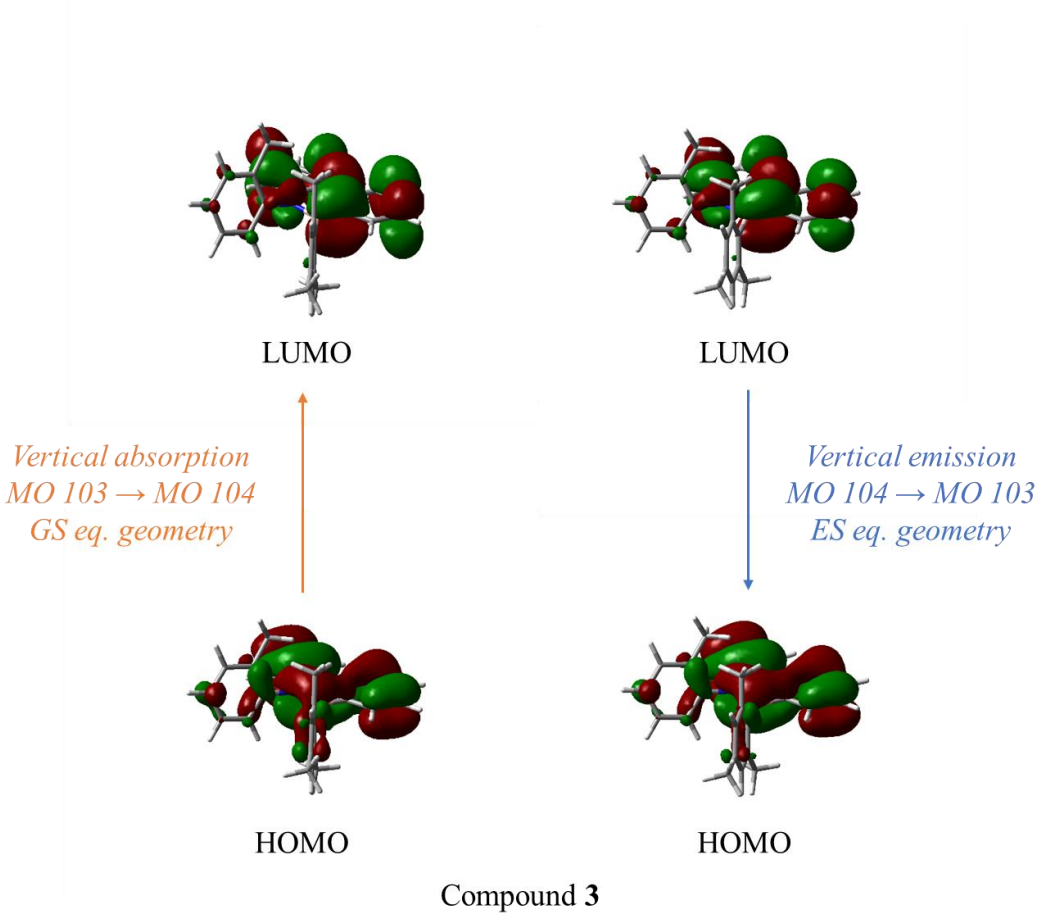


*Figure 23 Plots of the MOs contributing the most to the vertical absorption and emission related to the 1st excited state for GS1 conformation of compound **3** in THF*

From Figure 23, it is already clear that the GS and ES equilibrium geometries are almost identical, which can be better perceived by the very similar dihedral angle values (Figure 24).

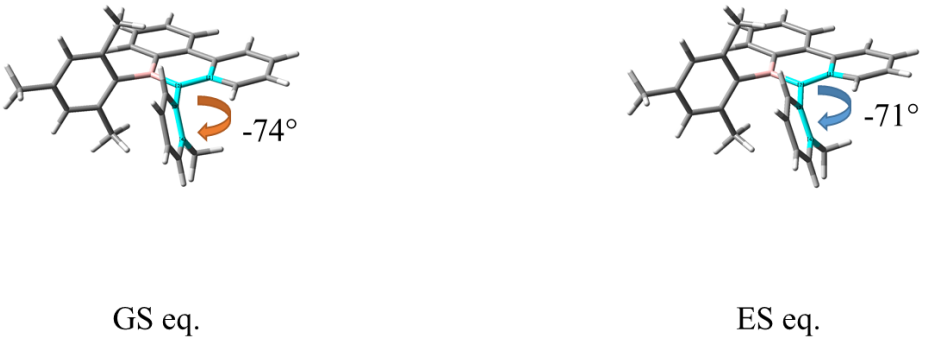
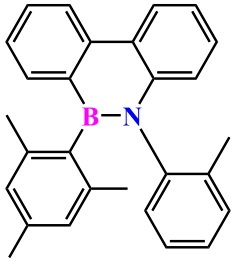


*Figure 24 Almost identical GS_{eq} and ES_{eq} structures for GS1 conformation of compound **3** in THF*

This indicates that no significant intramolecular relaxation process occurred and therefore the Stokes shift value is expected to be rather small as a result of the small difference between the absorption and emission energies. The latter is confirmed by the results obtained (Table 7).

Table 7



3

Ground State	Solvent	$E_{absorption}$	$E_{emission}$	Stokes Shift
GS1	*n*-hexane	4.479 eV	3.942 eV	37.730 nm
		276.822 nm	314.552 nm	
	THF	4.482 eV	3.919 eV	39.725 nm
		276.618 nm	316.343 nm	
	acetonitrile	4.486 eV	3.912 eV	40.556 nm
		276.384 nm	316.940 nm	
GS2	*n*-hexane	4.490 eV	4.010 eV	33.063 nm
		276.108 nm	309.170 nm	
	THF	4.493 eV	3.986 eV	35.099 nm
		275.943 nm	311.042 nm	
	acetonitrile	4.497 eV	3.976 eV	36.109 nm
		275.714 nm	311.823 nm	

For compound **4**, for all four ground states and in all three solvents, the major orbital transition contributing to the excitation and emission to and from the first excited state is the MO (108) - MO (109), corresponding to the HOMO – LUMO (Figure 25).

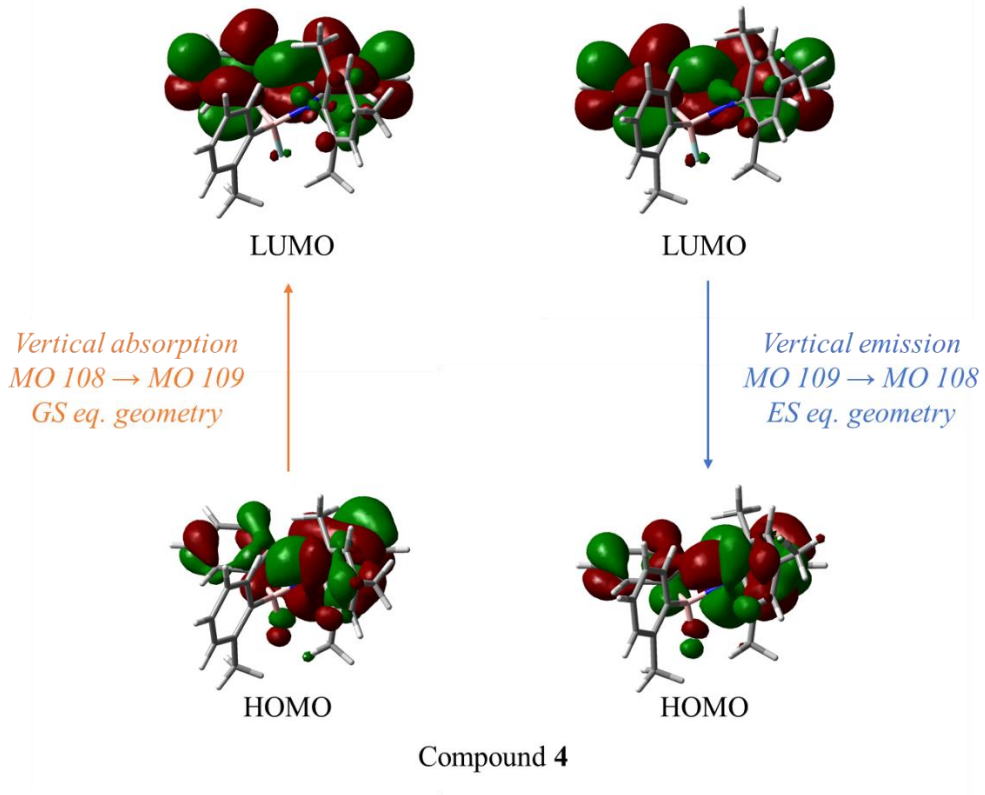


*Figure 25 Figure 26 Plots of the MOs contributing the most to the vertical absorption and emission related to the 1st excited state for GS1-0-R conformation of compound **4** in THF*

From Figure 25, it is evident that a slight geometrical relaxation from GS to ES structures occurs (dihedral angle values in Figure 27) along with an intramolecular charge transfer from the right half of the molecule where the nitrogen atom and mesityl moiety lie towards the electron-deficient half comprising of the boron atom and the left part of the phenanthrene unit. In this case, a clear donor-acceptor pair exists, which is expected to give rise to a noticeable solvatochromic effect. Indeed, the aforementioned are summarized by the Stokes shift values presented in Table 8. For GS1-180-R in *n*-hexane no results could be obtained, due to a convergence error that occurred during the calculation.

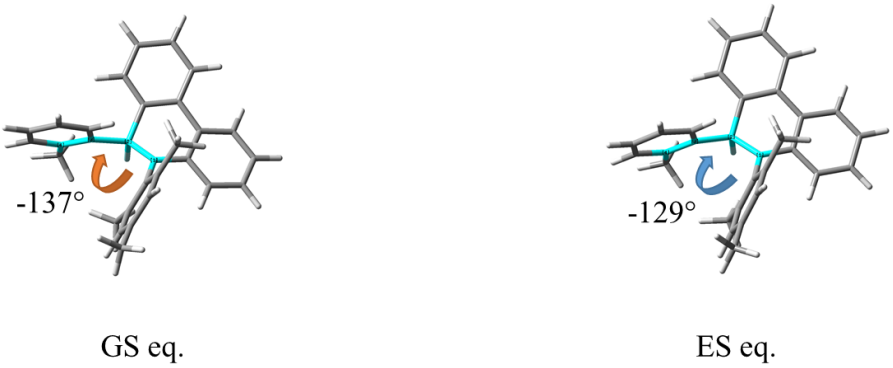
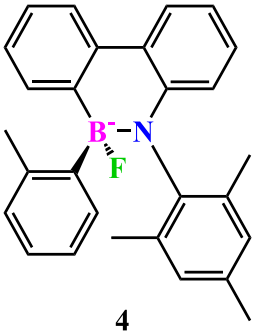


*Figure 27 Dihedral angle difference between GS_{eq} and ES_{eq} structures for GS1-0-R conformation of compound **4** in THF*

Table 8



4

Ground State	Solvent	$E_{absorption}$	$E_{emission}$	Stokes Shift
GS1-0-R	*n*-hexane	3.863 eV	3.366 eV	47.438 nm
		320.914 nm	368.352 nm	
	THF	3.866 eV	3.289 eV	56.334 nm
		320.678 nm	377.012 nm	
	acetonitrile	3.880 eV	3.254 eV	61.469 nm
		319.555 nm	381.024 nm	
GS1-180-R	*n*-hexane	-	-	-
		-	-	
	THF	3.853 eV	3.266 eV	57.854 nm
		321.746 nm	379.601 nm	
	acetonitrile	3.868 eV	3.228 eV	63.545 nm
		320.578 nm	384.123 nm	
GS2-0-R	*n*-hexane	3.749 eV	3.188 eV	58.204 nm
		330.751 nm	388.955 nm	
	THF	3.765 eV	3.119 eV	68.252 nm
		329.318 nm	397.571 nm	

	acetonitrile	3.811 eV	3.082 eV	77.007 nm
		325.322 nm	402.329 nm	
GS2-180-R	*n*-hexane	3.721 eV	3.242 eV	49.232 nm
		333.195 nm	382.427 nm	
	THF	3.751 eV	3.178 eV	59.575 nm
		330.574 nm	390.149 nm	
	acetonitrile	3.779 eV	3.154 eV	65.017 nm
		328.084 nm	393.101 nm	

In general, the Stokes shift values as derived for all four compounds are not significantly large. Yet, an interesting observation arises from the increase of Stokes shift when the substituents on the boron and nitrogen centers are exchanged from compound **2** to **3**. This could be attributed to the fact that the more electron-donating mesityl group when attached to the electron-deficient boron instead of the nitrogen atom, stabilizes better the HOMO, broadening the HOMO-LUMO gap. Stabilization of the HOMO is also the cause that compound **4** exhibits the largest Stokes shift in comparison to the other three studied compounds. These two cases are an indication of the effect of the substituents on the adjustment of the HOMO-LUMO gap (along with the solvent effect) and the resulting wavelength range of the emitted radiation and Stokes shift value.

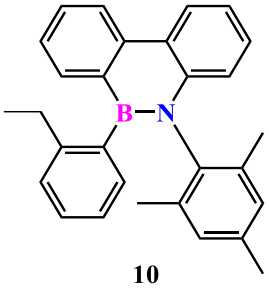
Even though the Stokes shift values are overall rather small, in all four cases, an increase in the Stokes shift is observed with the gradual increase of the solvent polarity from *n*-hexane to THF and then to acetonitrile. This trend is compatible with the positive solvatochromic effect (a gradual increase of the solvent polarity results in a red-shift) and implies that the excited states are characterized by a larger charge separation in comparison to the corresponding ground states and are therefore better stabilized by more polar solvents.

3.2 Synthesis and characterization

The syntheses tackled in this thesis were inspired by the work of two independent groups[1,7].

Based on the aforementioned works and with a special interest and focus towards the incorporation of substituents on the boron and nitrogen centers that could potentially afford atropisomeric

structures, the synthesis of compound **10** was attempted in two different ways (leading to **10a** and **10b**). Compound **10** is similar to the theoretically studied compound **2**, but contrary to the latter, a 2-ethylphenyl substituent was introduced in the boron center instead of the *o*-tolyl, in order to act as a chirality probe for NMR detection.



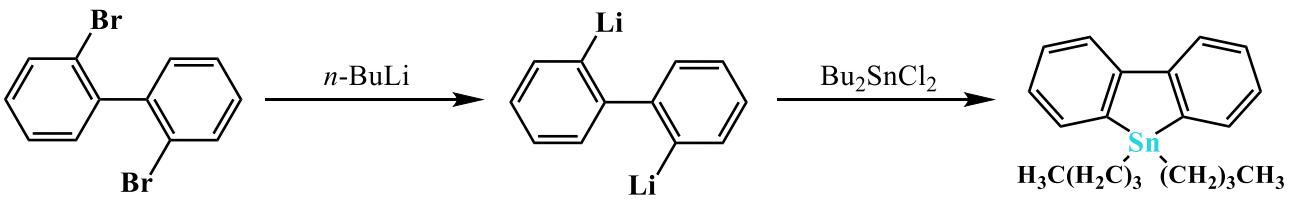
10

Figure 28 The target compound

As in the previous works[1,7], the main synthetic concept evolved around the obtention of the anti-aromatic 9-borafluorene precursors by boron-tin exchange from the reaction of a 9-stannafluorene derivative with boron reagents, followed by an aromaticity-driven ring-opening reaction between the borafluorene precursors and an organic azide.

Inert conditions are an important key point in the synthetic procedures followed. Since no glovebox equipment was available, reactions were prone to the impact of air and moisture, even though all possible precautions were taken (Schlenk line for N_2 and vacuum atmosphere, dried glassware, dry solvents).

The first step involved the formation of stannafluorene from 2,2'-dibromobiphenyl through a 2,2-dilithiobiphenyl intermediate. The general concept applied was based upon a similar previous work[1], but the reagents, their proportions and the experimental conditions were modified. In a first attempt, two equiv. of *n*-BuLi were used and the reaction afforded many by-products and the desired product **5** only in traces, whereas in the second attempt, an excess of *n*-BuLi (2.2 eq.) was used and **5** was obtained with 25.6% yield.

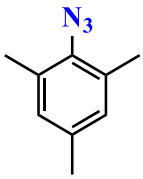


5

Scheme 1 Formation of the 9,9-dibutyl-9-stannafluorene

The organic azide selected as suitable to take part in the next step of the synthetic procedure was the symmetric and sterically hindered 2-azido-1,3,5-trimethylbenzene (mesitylazide) **8**. For its synthesis,

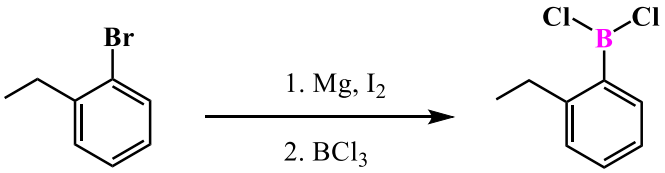
an efficient procedure previously developed[25] was employed starting from 2,4,6-trimethylaniline and affording the desired azide in 90%.



8

*Figure 29 The selected azide **8***

The conversion of 1-bromo-2-ethylbenzene to a Grignard reagent and eventually to a borane derivative was freshly done; 1-bromo-2-ethylbenzene was added to the solvent (3mL of dry Et_2O), in which 6 equiv. of activated magnesium and a tip of iodine that plays the role of the indicator of the beginning of the reaction when it turns from purplish to colorless were also present and was heated to reflux for 2 hours. Afterwards, 3 equiv. of BCl_3 were dissolved in 5 mL of dry toluene in a second flask and the Grignard reagent was added at -78°C, stirred and left to react for 12 hours at room temperature. The outcome of the reaction was monitored by the consumption of the solid Mg and the de-colorization of I_2, as well as by ^{1}H and ^{11}B NMR.

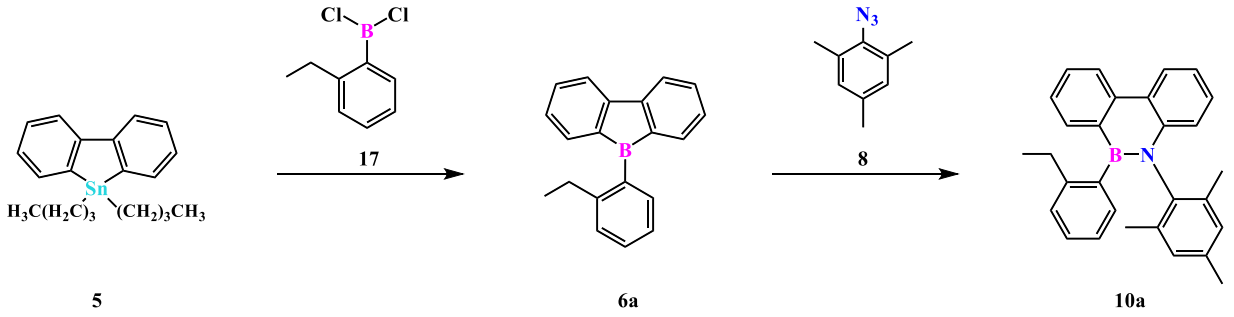


17

*Scheme 2 Grignard reagent formation and its conversion to a borane derivative (**17**)*

The boron-tin exchange and the ring-opening reaction were performed in a one-pot process. Stannafluorene **5** was added dropwise to the freshly prepared **17** at -78°C and the reaction solution was let to stir overnight at room temperature. Then, azide **8** was added dropwise at -78°C and after the solution had reached room temperature, it was heated to reflux and was let to react overnight. After column chromatography purification of the crude, the fractions obtained were characterized by

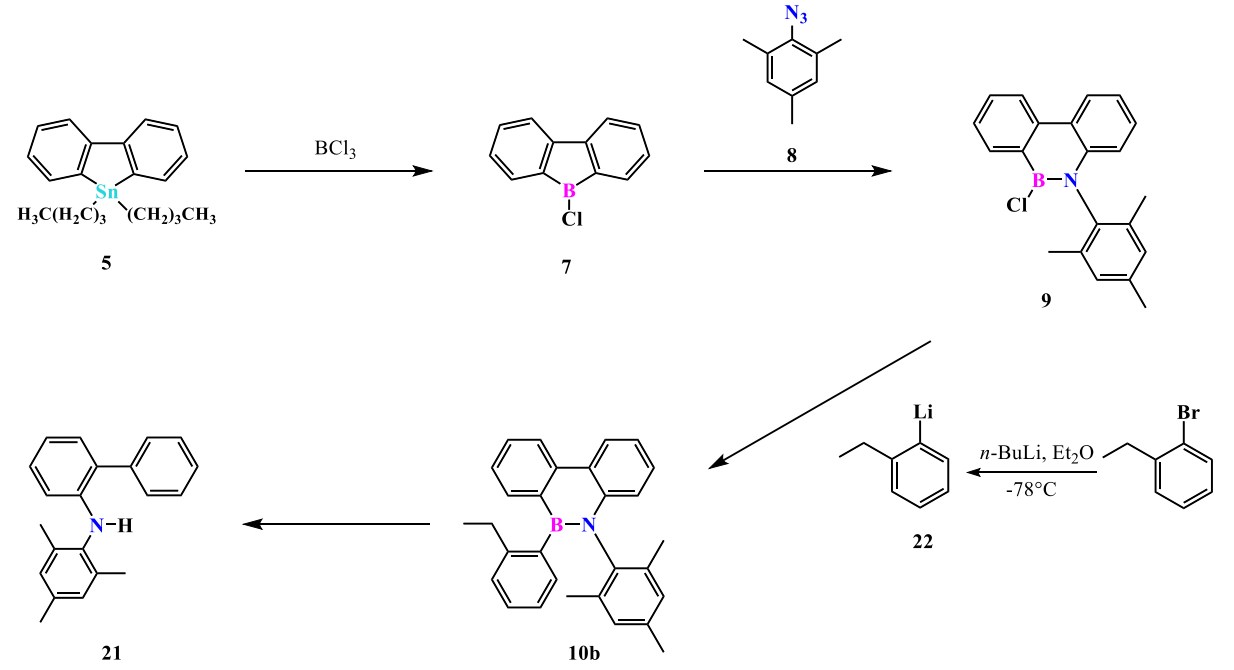
^{1}H and ^{11}B NMR and the results revealed that the expected product was not formed; instead, a combination of reactants, intermediates and by-products was obtained.



*Scheme 3 One-pot synthesis towards **10a***

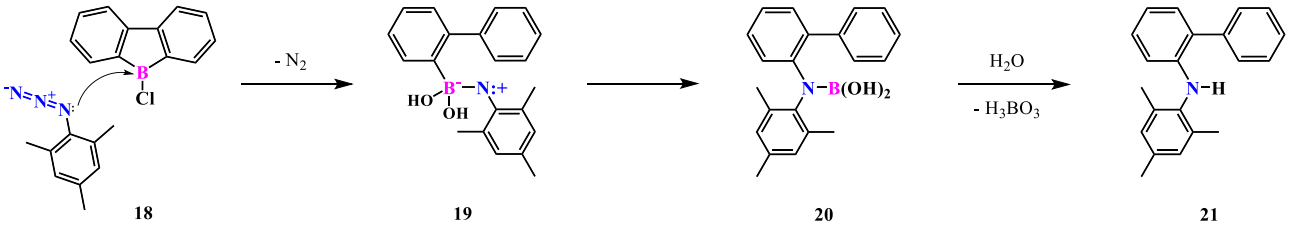
Next, another synthetic scheme was followed; instead of the direct introduction of a substituent on the boron, in this scheme, a highly moisture-sensitive 9-chloro-9-borafluorene was first synthesized. For this purpose, BCl_3 was added dropwise in a solution of 9-stannafluorene **5** at 0°C and the solution was stirred for 22 hours at room temperature. The Bu_2SnCl_2 by-product was removed by sublimation to give a yellow solid residue and then the azide **8** was added dropwise at 0°C. After the solution had reached room temperature, it was heated to reflux and was let stirring overnight.

In a second flask, 1-bromo-2-ethylbenzene in dry Et_2O was cooled at -78°C, upon which *n*-BuLi was added dropwise and afforded the lithiated derivative **22** after 1 hour of stirring at room temperature. Afterwards, **22** was added dropwise at -78°C in the solution of **9**. The reaction solution was stirred at this temperature for 1 hour and was then let to stir at room temperature for another 3 hours. Column chromatography of the crude afforded **21** in 12.4% yield, instead of the expected product **10b.**



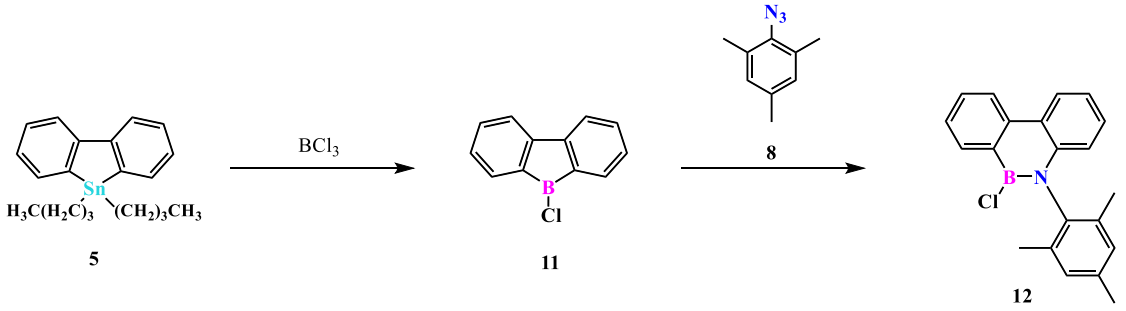
*Scheme 4 One-pot synthesis towards **10b** led to the formation of **21** instead*

Based on the reaction pathways introduced in previous works[9,26], the proposed mechanism for the formation of compound **21** as a result of a rearrangement is illustrated in Scheme 5. The α-nitrogen of the azide attacks the boron of 9-chloro-9-borafluorene and after N_2 expulsion and coordination of two hydroxyl groups from the inevitable present moisture, the intermediate **19** forms, which is rearranged into **20**. In the last step, boronic acid is released and the open product **21** is obtained.



*Scheme 5 Proposed mechanism for the formation of **21***

In order to confirm the first two steps of the reaction, the same synthetic procedure was repeated until the stage of the ring-opening reaction. BCl_3 was added dropwise in a solution of 9-stannafluorene **5** at 0°C and the solution was stirred for 27 hours at room temperature. The sublimation of the Bu_2SnCl_2 by-product was skipped and the azide **8** was added dropwise at 0°C directly. After the solution had reached room temperature, it was heated to reflux and was let stirring for 19 hours after which the reaction was quenched with MeOH. NMR showed signals of the starting materials and intermediates, but not of the product.



Scheme 6 Repetition of the first two steps of the reaction

4 Conclusions / Further Studies

In the framework of this thesis, a theoretical study of the compounds **1**, **2**, **3** and **4** was performed by means of DFT and TD-DFT, while an experimental synthesis of compound **10** was attempted.

Conformational search revealed all the possible ground and transition states for all four compounds computationally studied and an atropisomeric nature was validated for compounds **1**, **2** and **3** as the energy barrier for the interconversion of the atropisomers was found in all three cases to be higher than 25 kcal/mol. In the theoretical simulation of ECD spectra, the weighed ECD spectrum of compound **2** would be trivial to be compared with an experimental spectrum due to its sensitivity to the ground state populations, while the ECD spectrum of compound **3** is more suitable in that sense to be used as reference. In the context of the 7-step computational cycle for the study of UV-Vis absorption and fluorescence emission, the results obtained reveal a positive solvatochromic effect and in increase in the Stokes shift values when donor substituents are attached to the electron-deficient boron atom. In the future, these trends could be further explored with different substitutions.

The experimental synthesis of compound **10** did not afford the expected product in both procedures followed. Instead, the open structure **21** was obtained, for the formation of which a mechanism was proposed. A future task could be the verification of the repeatability of the open structure obtained, as ring-closure towards the desired product **10** can be achieved from **21** through a Friedel-Crafts reaction with BCl_3 and $AlCl_3$, followed by a nucleophilic attack of a freshly formed Grignard reagent. Ideally, all reactions should be performed again with a glovebox - or at least under argon atmosphere - due to the air- and moisture-sensitive nature of the reagents and intermediates involved.

5 Experimental Section

5.1 TD-DFT fluorescence calculations

5.1.1 Compound 1

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1043.78822544 a.u.
Lowest frequency = 15.3183

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.198520	0.761266	-0.072179
2	5	0	0.015792	-0.642184	-0.123470
3	6	0	-1.238931	-1.538220	-0.134988
4	6	0	-1.127240	-2.938359	-0.192386
5	1	0	-0.135668	-3.379023	-0.233587
6	6	0	-2.241936	-3.753452	-0.199266
7	6	0	-3.509204	-3.168581	-0.150837
8	1	0	-4.396841	-3.794421	-0.156109
9	6	0	-3.647517	-1.794783	-0.098262
10	1	0	-4.648372	-1.382288	-0.063583
11	6	0	-2.520775	-0.953233	-0.089510
12	6	0	-2.638945	0.512319	-0.039632
13	6	0	-3.891916	1.145678	0.001679
14	1	0	-4.790859	0.542159	-0.000739
15	6	0	-1.636084	2.729319	0.007501
16	1	0	-0.755716	3.357699	0.008821
17	6	0	-4.028289	2.518630	0.044781
18	1	0	-5.016077	2.966557	0.075791
19	6	0	-2.886156	3.315300	0.046775
20	6	0	-1.488278	1.334318	-0.034688
21	6	0	2.130650	-1.757083	0.938990
22	6	0	1.473969	-1.242724	-0.194901
23	6	0	2.123099	-1.327503	-1.431276
24	1	0	1.627728	-0.944032	-2.320241
25	6	0	1.481492	2.127102	-1.225804
26	6	0	1.462432	2.056582	1.181875
27	6	0	0.927207	1.659141	-0.039002
28	6	0	2.577780	2.980921	-1.190499
29	1	0	3.010730	3.338231	-2.119512
30	6	0	3.119462	3.373195	0.029063
31	6	0	2.559039	2.910538	1.214731
32	1	0	2.976248	3.213290	2.169961
33	6	0	3.386608	-1.893551	-1.560001
34	1	0	3.864124	-1.945748	-2.533948
35	6	0	4.028446	-2.392301	-0.434402
36	1	0	5.015075	-2.838811	-0.516481
37	6	0	3.398302	-2.321918	0.802595
38	1	0	3.899121	-2.715483	1.683541

39	1	0	-2.137807	-4.833093	-0.243430
40	1	0	-2.968494	4.397193	0.078807
41	6	0	1.484694	-1.689642	2.301389
42	1	0	0.458734	-2.070976	2.280656
43	1	0	1.437070	-0.657746	2.667874
44	1	0	2.045840	-2.272992	3.036495
45	1	0	1.049887	1.816415	-2.171697
46	1	0	3.976875	4.038173	0.055201
47	1	0	1.011620	1.696798	2.101240

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 4.4755 eV 277.03 nm f=0.2572
<S**2>=0.000

90 -> 92	0.11409
90 -> 93	0.20524
91 -> 92	0.62123
91 -> 93	-0.13930

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1043.85161783 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1043.68632213 a.u.

Excited State 1: Singlet-A 4.4996 eV 275.55 nm f=0.1667
<S**2>=0.000

90 -> 92	0.12676
90 -> 93	0.23143
91 -> 92	0.60384
91 -> 93	-0.14446

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1043.62918608 a.u.
Lowest frequency = 16.5671

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.200376	0.796894	0.015947
2	5	0	0.024095	-0.668685	-0.089005
3	6	0	-1.206828	-1.522702	-0.202507
4	6	0	-1.136720	-2.915265	-0.389706
5	1	0	-0.155116	-3.378451	-0.443296
6	6	0	-2.264915	-3.710766	-0.520368
7	6	0	-3.545099	-3.115805	-0.473899
8	1	0	-4.435647	-3.728671	-0.567866

9	6	0	-3.664962	-1.752169	-0.310391
10	1	0	-4.661005	-1.327409	-0.270964
11	6	0	-2.523739	-0.908866	-0.179638
12	6	0	-2.644733	0.496412	-0.011937
13	6	0	-3.898047	1.173289	0.004329
14	1	0	-4.801843	0.611921	-0.190287
15	6	0	-1.608503	2.706740	0.478264
16	1	0	-0.726079	3.300491	0.672710
17	6	0	-4.006026	2.522597	0.274356
18	1	0	-4.987311	2.986134	0.295264
19	6	0	-2.861059	3.296598	0.536720
20	6	0	-1.454381	1.340599	0.160232
21	6	0	2.039396	-1.995250	0.919010
22	6	0	1.493965	-1.229229	-0.131770
23	6	0	2.283156	-1.014283	-1.269471
24	1	0	1.884165	-0.418440	-2.086469
25	6	0	1.112954	2.489922	-1.159613
26	6	0	1.823400	1.748902	1.023752
27	6	0	0.918761	1.693329	-0.031886
28	6	0	2.213270	3.333995	-1.230531
29	1	0	2.364620	3.945785	-2.114251
30	6	0	3.121136	3.389562	-0.176523
31	6	0	2.922784	2.596754	0.948083
32	1	0	3.627110	2.634631	1.772984
33	6	0	3.563111	-1.541644	-1.388861
34	1	0	4.145875	-1.360766	-2.287161
35	6	0	4.089292	-2.296063	-0.348287
36	1	0	5.090034	-2.711772	-0.421364
37	6	0	3.328845	-2.512614	0.794883
38	1	0	3.745587	-3.094267	1.613300
39	1	0	-2.166480	-4.782280	-0.661954
40	1	0	-2.952750	4.349196	0.780517
41	6	0	1.257866	-2.256397	2.185161
42	1	0	0.422451	-2.941989	2.010953
43	1	0	0.826855	-1.335810	2.593232
44	1	0	1.896411	-2.697074	2.955986
45	1	0	0.401020	2.435306	-1.977028
46	1	0	3.982256	4.047633	-0.233930
47	1	0	1.664442	1.125104	1.896614

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1043.69481550 a.u.

Excited State 1: Singlet-A 3.9830 eV 311.28 nm f=0.2346
<S**2>=0.000
90 -> 93 -0.19437
91 -> 92 0.65126

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1043.84111304 a.u.

Results

Absorb Energy =	0.165 a.u.	4.498 eV	275.647 nm

Emission Energy =	0.146 a.u.	3.981 eV	311.443 nm
Stokes Shift =	0.019 a.u.	0.517 eV	35.796 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1043.79200533 a.u.
Lowest frequency = 18.4145

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.197806	0.761688	-0.067498
2	5	0	0.015066	-0.641577	-0.119799
3	6	0	-1.240704	-1.536941	-0.134027
4	6	0	-1.131435	-2.937539	-0.192547
5	1	0	-0.140794	-3.380736	-0.229588
6	6	0	-2.247420	-3.751379	-0.204901
7	6	0	-3.514450	-3.164548	-0.161354
8	1	0	-4.402918	-3.788908	-0.171456
9	6	0	-3.650846	-1.790228	-0.107300
10	1	0	-4.651335	-1.376726	-0.076629
11	6	0	-2.522315	-0.950435	-0.092247
12	6	0	-2.638911	0.515304	-0.038946
13	6	0	-3.891979	1.149559	0.002560
14	1	0	-4.791931	0.547583	-0.002577
15	6	0	-1.633525	2.731124	0.017522
16	1	0	-0.752904	3.359091	0.023094
17	6	0	-4.026748	2.522897	0.049887
18	1	0	-5.014021	2.971783	0.080886
19	6	0	-2.883305	3.318530	0.056712
20	6	0	-1.486867	1.335847	-0.029765
21	6	0	2.128207	-1.767585	0.937322
22	6	0	1.473125	-1.243289	-0.193421
23	6	0	2.124562	-1.316301	-1.429905
24	1	0	1.631539	-0.923220	-2.315907
25	6	0	1.474835	2.134037	-1.224557
26	6	0	1.473738	2.046970	1.183823
27	6	0	0.929192	1.659014	-0.036178
28	6	0	2.572612	2.986667	-1.191512
29	1	0	2.998583	3.350305	-2.121228
30	6	0	3.123950	3.370067	0.027110
31	6	0	2.571874	2.899838	1.214168
32	1	0	2.996174	3.195891	2.168288
33	6	0	3.388838	-1.881175	-1.561760
34	1	0	3.868182	-1.923986	-2.535256
35	6	0	4.029208	-2.390078	-0.439198
36	1	0	5.016205	-2.835295	-0.523605
37	6	0	3.396861	-2.330782	0.797828
38	1	0	3.896645	-2.731650	1.676005
39	1	0	-2.144791	-4.831081	-0.249570
40	1	0	-2.964445	4.400318	0.092719
41	6	0	1.480111	-1.713112	2.299385

42	1	0	0.460332	-2.110629	2.276218
43	1	0	1.414807	-0.683077	2.668045
44	1	0	2.049682	-2.289252	3.033496
45	1	0	1.036523	1.830531	-2.169742
46	1	0	3.981848	4.034396	0.051355
47	1	0	1.030291	1.681959	2.104730

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 4.4736 eV 277.15 nm f=0.2625
<S**2>=0.000
90 -> 92 0.10586
90 -> 93 0.20586
91 -> 92 0.62456
91 -> 93 -0.13012

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1043.85565029 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1043.69032509 a.u.

Excited State 1: Singlet-A 4.4989 eV 275.59 nm f=0.1661
<S**2>=0.000
90 -> 92 0.11866
90 -> 93 0.23367
91 -> 92 0.60667
91 -> 93 -0.13468

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1043.63499243 a.u.
Lowest frequency = 19.8276

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.199759	0.794705	0.005295
2	5	0	0.017146	-0.669616	-0.090700
3	6	0	-1.218441	-1.520888	-0.185466
4	6	0	-1.156834	-2.914563	-0.348913
5	1	0	-0.178290	-3.385450	-0.394583
6	6	0	-2.290114	-3.708120	-0.463604
7	6	0	-3.567725	-3.104439	-0.424051
8	1	0	-4.461506	-3.714273	-0.506812
9	6	0	-3.681106	-1.739590	-0.281768
10	1	0	-4.675026	-1.309723	-0.249262
11	6	0	-2.532109	-0.896931	-0.165309

12	6	0	-2.647569	0.506645	-0.020300
13	6	0	-3.902332	1.190140	-0.007852
14	1	0	-4.810211	0.628742	-0.181125
15	6	0	-1.597155	2.724223	0.413183
16	1	0	-0.712151	3.321652	0.582006
17	6	0	-3.999906	2.543879	0.232601
18	1	0	-4.978249	3.013774	0.250943
19	6	0	-2.848293	3.319810	0.465812
20	6	0	-1.450371	1.350698	0.132884
21	6	0	2.048713	-1.977110	0.913601
22	6	0	1.484896	-1.235979	-0.145007
23	6	0	2.251607	-1.050503	-1.303276
24	1	0	1.837239	-0.475363	-2.127528
25	6	0	1.184488	2.429486	-1.174301
26	6	0	1.779557	1.776279	1.071335
27	6	0	0.929714	1.682110	-0.025975
28	6	0	2.293863	3.264248	-1.224454
29	1	0	2.493185	3.838888	-2.123344
30	6	0	3.148449	3.358384	-0.129264
31	6	0	2.888441	2.614190	1.016403
32	1	0	3.550213	2.683786	1.873796
33	6	0	3.529544	-1.581780	-1.433763
34	1	0	4.095270	-1.423963	-2.347177
35	6	0	4.075341	-2.310370	-0.384259
36	1	0	5.074534	-2.728140	-0.465625
37	6	0	3.336038	-2.498361	0.778181
38	1	0	3.767742	-3.060266	1.602533
39	1	0	-2.197506	-4.782399	-0.586606
40	1	0	-2.934410	4.379186	0.680910
41	6	0	1.288806	-2.210328	2.198154
42	1	0	0.456468	-2.906743	2.053639
43	1	0	0.858452	-1.282353	2.589377
44	1	0	1.941892	-2.627510	2.969640
45	1	0	0.513911	2.345816	-2.023587
46	1	0	4.015799	4.009374	-0.170245
47	1	0	1.570213	1.193327	1.961923

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1043.69912782 a.u.

Excited State 1: Singlet-A 3.9758 eV 311.84 nm f=0.2413
<S**2>=0.000
90 -> 93 -0.19186
91 -> 92 0.65158

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1043.84488763 a.u.

Results

Absorb Energy =	0.165 a.u.	4.499 eV	275.598 nm
Emission Energy =	0.146 a.u.	3.966 eV	312.592 nm

```
     Stokes Shift      =  | 0.020 a.u. | 0.532 eV | 36.994 nm
 ---------------------------------------------------------------------
```

Acetonitrile

Step1

```
 Method: cam-b3lyp/6-31G(d)
 Solvent : Acetonitrile
 SCF Done: E(RCAM-B3LYP) = -1043.79360930 a.u.
 Lowest frequency =  20.2383
```

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.197222	0.761777	-0.064357
2	5	0	0.014947	-0.641383	-0.117701
3	6	0	-1.241306	-1.536322	-0.134424
4	6	0	-1.133362	-2.937075	-0.194869
5	1	0	-0.143247	-3.381670	-0.229917
6	6	0	-2.250018	-3.750122	-0.211303
7	6	0	-3.516848	-3.162245	-0.170357
8	1	0	-4.405778	-3.785763	-0.183991
9	6	0	-3.652182	-1.787766	-0.114313
10	1	0	-4.652448	-1.373688	-0.085903
11	6	0	-2.522754	-0.948960	-0.094587
12	6	0	-2.638588	0.516812	-0.037958
13	6	0	-3.891620	1.151558	0.004456
14	1	0	-4.792077	0.550414	-0.002640
15	6	0	-1.631904	2.731901	0.025965
16	1	0	-0.751207	3.359699	0.034620
17	6	0	-4.025534	2.524974	0.055550
18	1	0	-5.012535	2.974326	0.087099
19	6	0	-2.881465	3.320001	0.065838
20	6	0	-1.485917	1.336587	-0.025799
21	6	0	2.125759	-1.775979	0.936319
22	6	0	1.473040	-1.243549	-0.192282
23	6	0	2.127222	-1.307483	-1.428046
24	1	0	1.636388	-0.907514	-2.312151
25	6	0	1.467695	2.141493	-1.223927
26	6	0	1.482582	2.039223	1.184316
27	6	0	0.930161	1.659035	-0.034640
28	6	0	2.565457	2.994505	-1.192796
29	1	0	2.984780	3.364491	-2.122990
30	6	0	3.125031	3.370159	0.024749
31	6	0	2.581133	2.892036	1.212632
32	1	0	3.011591	3.182262	2.165741
33	6	0	3.392135	-1.871201	-1.561299
34	1	0	3.873528	-1.906857	-2.534053
35	6	0	4.030275	-2.388069	-0.440841
36	1	0	5.017582	-2.832352	-0.526220
37	6	0	3.395129	-2.337856	0.795414
38	1	0	3.893259	-2.744884	1.671659
39	1	0	-2.148203	-4.829812	-0.257214
40	1	0	-2.961960	4.401676	0.105323
41	6	0	1.475252	-1.731271	2.297637
42	1	0	0.456573	-2.131270	2.270128
43	1	0	1.406273	-0.703725	2.672503
44	1	0	2.045101	-2.310418	3.029044

45	1	0	1.023555	1.843862	-2.168269
46	1	0	3.982662	4.034839	0.047514
47	1	0	1.045748	1.668554	2.106116

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 4.4777 eV 276.89 nm f=0.2487
<S**2>=0.000
90 -> 92 0.10557
90 -> 93 0.21006
91 -> 92 0.62272
91 -> 93 -0.12889

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1043.85736276 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1043.69196247 a.u.

Excited State 1: Singlet-A 4.4997 eV 275.54 nm f=0.1655
<S**2>=0.000
90 -> 92 0.11656
90 -> 93 0.23442
91 -> 92 0.60703
91 -> 93 -0.13261

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1043.63747412 a.u.
Lowest frequency = 17.9514

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.199156	0.793314	-0.001139
2	5	0	0.013520	-0.670042	-0.092780
3	6	0	-1.224665	-1.519770	-0.177489
4	6	0	-1.167625	-2.913983	-0.327878
5	1	0	-0.190782	-3.388908	-0.369862
6	6	0	-2.303836	-3.706218	-0.432939
7	6	0	-3.579864	-3.098084	-0.396572
8	1	0	-4.475446	-3.706160	-0.472493
9	6	0	-3.689631	-1.732449	-0.265908
10	1	0	-4.682398	-1.299932	-0.236187
11	6	0	-2.536695	-0.890582	-0.158308
12	6	0	-2.648687	0.512345	-0.025411
13	6	0	-3.903740	1.199401	-0.015198

14	1	0	-4.813642	0.638254	-0.177800
15	6	0	-1.591015	2.732533	0.378708
16	1	0	-0.704673	3.331358	0.534601
17	6	0	-3.996235	2.555307	0.209642
18	1	0	-4.973038	3.028470	0.226215
19	6	0	-2.841285	3.331537	0.427936
20	6	0	-1.448159	1.355781	0.117809
21	6	0	2.052923	-1.967921	0.909985
22	6	0	1.480151	-1.239731	-0.152731
23	6	0	2.236161	-1.069430	-1.320478
24	1	0	1.814244	-0.505373	-2.148613
25	6	0	1.223294	2.396572	-1.180267
26	6	0	1.755036	1.791525	1.094852
27	6	0	0.935343	1.675975	-0.023085
28	6	0	2.337351	3.226282	-1.218771
29	1	0	2.562963	3.780526	-2.124177
30	6	0	3.162624	3.341508	-0.103241
31	6	0	2.868701	2.624194	1.051629
32	1	0	3.507038	2.711160	1.925039
33	6	0	3.513414	-1.602031	-1.455345
34	1	0	4.070945	-1.456124	-2.375745
35	6	0	4.068744	-2.316953	-0.401170
36	1	0	5.067342	-2.735397	-0.485863
37	6	0	3.339412	-2.490660	0.769979
38	1	0	3.778281	-3.042370	1.597384
39	1	0	-2.214378	-4.781869	-0.545586
40	1	0	-2.924199	4.394125	0.628102
41	6	0	1.303124	-2.186913	2.202882
42	1	0	0.474660	-2.890990	2.073402
43	1	0	0.869717	-1.256013	2.583471
44	1	0	1.963647	-2.589026	2.975901
45	1	0	0.575616	2.296720	-2.045403
46	1	0	4.033216	3.988632	-0.135093
47	1	0	1.518315	1.230524	1.992792

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1043.70089935 a.u.

Excited State 1: Singlet-A 3.9745 eV 311.95 nm f=0.2442
<S**2>=0.000
90 -> 93 -0.19078
91 -> 92 0.65133

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1043.84649342 a.u.

Results

Absorb Energy =	0.165 a.u.	4.501 eV	275.473 nm
Emission Energy =	0.146 a.u.	3.962 eV	312.948 nm
Stokes Shift =	0.020 a.u.	0.539 eV	37.475 nm

5.1.2 Compound 2 – GS1

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1161.66389478 a.u.
Lowest frequency = 23.9922

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.181309	-0.591023	-0.115615
2	5	0	0.621221	0.761872	-0.063218
3	6	0	2.144538	0.994175	0.042951
4	6	0	2.670504	2.290001	0.189509
5	1	0	1.986671	3.132736	0.183155
6	6	0	4.025379	2.509087	0.343467
7	6	0	4.892597	1.414758	0.357905
8	1	0	5.960066	1.568681	0.486172
9	6	0	4.403716	0.130577	0.213055
10	1	0	5.107546	-0.692394	0.239287
11	6	0	3.027554	-0.104906	0.046581
12	6	0	2.482145	-1.458213	-0.130502
13	6	0	3.322791	-2.577480	-0.247309
14	1	0	4.396063	-2.438896	-0.209866
15	6	0	0.600491	-2.976154	-0.390581
16	1	0	-0.467470	-3.137409	-0.459195
17	6	0	2.834851	-3.856548	-0.423462
18	1	0	3.519847	-4.693506	-0.510674
19	6	0	1.458073	-4.053651	-0.496398
20	6	0	1.086747	-1.672206	-0.203917
21	6	0	-1.104354	2.552466	0.886841
22	6	0	-0.368580	1.993591	-0.173464
23	6	0	-0.430275	2.632786	-1.420666
24	1	0	0.174498	2.252566	-2.240809
25	6	0	-2.015674	-0.862870	-1.201494
26	6	0	-1.433769	-0.530188	-2.549315
27	1	0	-2.069310	-0.925202	-3.346109
28	1	0	-1.357865	0.551572	-2.690832
29	1	0	-0.431682	-0.949277	-2.671775
30	6	0	-1.769017	-1.327496	1.177657
31	6	0	-1.224925	-0.917435	-0.048575
32	6	0	-0.906955	-1.546181	2.394115
33	1	0	-1.512643	-1.541706	3.303885
34	1	0	-0.399355	-2.515684	2.336728
35	1	0	-0.129917	-0.786719	2.493921
36	6	0	-3.374469	-1.153012	-1.089367
37	1	0	-3.991902	-1.108675	-1.983226
38	6	0	-3.957307	-1.504522	0.123422
39	6	0	-3.132965	-1.601159	1.241363
40	1	0	-3.559784	-1.909589	2.192737
41	6	0	-1.227313	3.749416	-1.643407
42	1	0	-1.253542	4.213888	-2.624648
43	6	0	-1.974392	4.270990	-0.595512

44	1	0	-2.599549	5.146162	-0.746190
45	6	0	-1.897817	3.677915	0.657779
46	1	0	-2.460179	4.101571	1.486138
47	6	0	-5.436455	-1.770317	0.225839
48	1	0	-5.657638	-2.508150	1.002323
49	1	0	-5.983503	-0.855108	0.480298
50	1	0	-5.842135	-2.139431	-0.720285
51	1	0	4.412846	3.516823	0.456709
52	1	0	1.050389	-5.048950	-0.643089
53	6	0	-1.052255	1.970358	2.276821
54	1	0	-0.049507	1.609522	2.526097
55	1	0	-1.741614	1.126093	2.378619
56	1	0	-1.332793	2.716203	3.026017

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 4.4556 eV 278.27 nm f=0.2533
<S**2>=0.000
102 ->105 0.18945
103 ->104 0.63044

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73507649 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57058829 a.u.

Excited State 1: Singlet-A 4.4778 eV 276.88 nm f=0.1652
<S**2>=0.000
102 ->105 0.21303
103 ->104 0.61496

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.50570501 a.u.
Lowest frequency = 19.6752

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.194658	-0.602376	-0.136011
2	5	0	0.635876	0.814903	-0.045640
3	6	0	2.117723	1.039731	0.084532
4	6	0	2.669719	2.324610	0.238990
5	1	0	1.997475	3.177527	0.234245
6	6	0	4.030093	2.540984	0.406687
7	6	0	4.913447	1.439634	0.432164
8	1	0	5.977655	1.595556	0.575719

9	6	0	4.421969	0.161022	0.274341
10	1	0	5.125077	-0.663089	0.297003
11	6	0	3.031470	-0.091031	0.086260
12	6	0	2.529551	-1.401068	-0.131238
13	6	0	3.367817	-2.550646	-0.214771
14	1	0	4.435254	-2.433749	-0.086687
15	6	0	0.622857	-2.937928	-0.576024
16	1	0	-0.437600	-3.089825	-0.725345
17	6	0	2.870580	-3.812342	-0.470277
18	1	0	3.553488	-4.653786	-0.531777
19	6	0	1.492469	-4.013805	-0.664773
20	6	0	1.087447	-1.636962	-0.285667
21	6	0	-1.215452	2.489691	0.869707
22	6	0	-0.386799	2.014309	-0.165152
23	6	0	-0.387522	2.723910	-1.376935
24	1	0	0.284136	2.407202	-2.171159
25	6	0	-2.026197	-0.818228	-1.183109
26	6	0	-1.475738	-0.412058	-2.523783
27	1	0	-2.160126	-0.709890	-3.322162
28	1	0	-1.340463	0.671088	-2.586369
29	1	0	-0.504641	-0.876180	-2.717198
30	6	0	-1.712076	-1.426249	1.158934
31	6	0	-1.205248	-0.940713	-0.056109
32	6	0	-0.815615	-1.684785	2.341749
33	1	0	-1.405397	-1.803279	3.253973
34	1	0	-0.236572	-2.603509	2.195502
35	1	0	-0.097694	-0.877207	2.499857
36	6	0	-3.379407	-1.124971	-1.051417
37	1	0	-4.021092	-1.032142	-1.924080
38	6	0	-3.926377	-1.554815	0.153037
39	6	0	-3.071635	-1.713257	1.241520
40	1	0	-3.471629	-2.078416	2.184310
41	6	0	-1.209138	3.823602	-1.594838
42	1	0	-1.185065	4.341838	-2.548899
43	6	0	-2.046567	4.258571	-0.576153
44	1	0	-2.692682	5.119167	-0.722750
45	6	0	-2.032743	3.598746	0.645851
46	1	0	-2.662905	3.958495	1.455505
47	6	0	-5.400298	-1.837675	0.279081
48	1	0	-5.594229	-2.636165	1.000946
49	1	0	-5.942659	-0.949091	0.622466
50	1	0	-5.833566	-2.132978	-0.680525
51	1	0	4.412624	3.549503	0.526987
52	1	0	1.107180	-5.003385	-0.884609
53	6	0	-1.224843	1.846572	2.233586
54	1	0	-0.228631	1.489427	2.511986
55	1	0	-1.905391	0.989805	2.266769
56	1	0	-1.551460	2.556113	2.999387

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.57893500 a.u.

Excited State 1: Singlet-A 4.0016 eV 309.84 nm f=0.2325
<S**2>=0.000
102 ->105 -0.18935
103 ->104 0.65119

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72593172 a.u.

Results

Absorb Energy =	0.164 a.u.	4.476 eV	277.001 nm
Emission Energy =	0.147 a.u.	4.000 eV	309.962 nm
Stokes Shift =	0.017 a.u.	0.476 eV	32.961 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1161.66722484 a.u.
Lowest frequency = 23.2283

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.184524	-0.592938	-0.113687
2	5	0	0.617629	0.761903	-0.067138
3	6	0	2.140298	1.002805	0.032442
4	6	0	2.661046	2.302299	0.167344
5	1	0	1.973352	3.141947	0.160435
6	6	0	4.016038	2.529620	0.310776
7	6	0	4.889257	1.439502	0.325484
8	1	0	5.956746	1.599630	0.444538
9	6	0	4.405833	0.151599	0.192135
10	1	0	5.114807	-0.666883	0.217237
11	6	0	3.029183	-0.091934	0.037672
12	6	0	2.489470	-1.449689	-0.124546
13	6	0	3.335616	-2.566510	-0.230264
14	1	0	4.408371	-2.423770	-0.194845
15	6	0	0.613967	-2.979107	-0.363566
16	1	0	-0.453278	-3.146785	-0.426961
17	6	0	2.852789	-3.849854	-0.391565
18	1	0	3.541346	-4.684637	-0.470353
19	6	0	1.476337	-4.054068	-0.459443
20	6	0	1.094590	-1.670690	-0.192832
21	6	0	-1.097061	2.553768	0.895138
22	6	0	-0.380598	1.987569	-0.175046
23	6	0	-0.471821	2.613577	-1.427358
24	1	0	0.116761	2.228315	-2.256708
25	6	0	-2.004903	-0.887233	-1.208041
26	6	0	-1.414233	-0.577089	-2.557736
27	1	0	-2.048573	-0.979174	-3.351751
28	1	0	-1.329750	0.501708	-2.715919
29	1	0	-0.414162	-1.003954	-2.669343
30	6	0	-1.771985	-1.316809	1.179556
31	6	0	-1.221271	-0.923456	-0.049121
32	6	0	-0.917499	-1.523920	2.403498

33	1	0	-1.525023	-1.485943	3.311117
34	1	0	-0.432103	-2.505955	2.369892
35	1	0	-0.124422	-0.779498	2.487871
36	6	0	-3.364644	-1.175611	-1.099965
37	1	0	-3.976541	-1.146469	-1.998205
38	6	0	-3.954928	-1.508340	0.115262
39	6	0	-3.136925	-1.588702	1.239460
40	1	0	-3.569178	-1.883337	2.192651
41	6	0	-1.279417	3.724140	-1.644726
42	1	0	-1.328895	4.177947	-2.630015
43	6	0	-2.007623	4.252837	-0.586538
44	1	0	-2.640638	5.123013	-0.733129
45	6	0	-1.901764	3.672922	0.671299
46	1	0	-2.449004	4.102261	1.506806
47	6	0	-5.434656	-1.773119	0.212902
48	1	0	-5.659550	-2.500427	0.998053
49	1	0	-5.982821	-0.854700	0.452905
50	1	0	-5.834815	-2.153635	-0.730948
51	1	0	4.399208	3.539894	0.415147
52	1	0	1.072864	-5.052777	-0.593462
53	6	0	-1.013516	1.986242	2.289821
54	1	0	-0.007106	1.622282	2.518661
55	1	0	-1.703871	1.146396	2.418188
56	1	0	-1.273016	2.741125	3.037387

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 4.4561 eV 278.24 nm f=0.2580
<S**2>=0.000
102 ->105 -0.18529
103 ->104 0.63142

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73868325 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57407838 a.u.

Excited State 1: Singlet-A 4.4793 eV 276.79 nm f=0.1643
<S**2>=0.000
102 ->105 -0.20872
103 ->104 0.61517

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51105136 a.u.
Lowest frequency = 18.1492

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.197648	-0.603325	-0.133050
2	5	0	0.631305	0.815135	-0.051010
3	6	0	2.113373	1.049436	0.069075
4	6	0	2.659311	2.336452	0.209279
5	1	0	1.983260	3.186621	0.202455
6	6	0	4.020663	2.563007	0.365036
7	6	0	4.910644	1.465366	0.391299
8	1	0	5.975271	1.628889	0.522991
9	6	0	4.426610	0.184067	0.249168
10	1	0	5.135245	-0.635137	0.271181
11	6	0	3.031937	-0.078889	0.075342
12	6	0	2.538629	-1.390799	-0.120120
13	6	0	3.384066	-2.541429	-0.183726
14	1	0	4.450087	-2.420192	-0.049375
15	6	0	0.637438	-2.940749	-0.549813
16	1	0	-0.422150	-3.100661	-0.696441
17	6	0	2.890817	-3.804872	-0.427766
18	1	0	3.575474	-4.645777	-0.476433
19	6	0	1.512840	-4.013691	-0.625915
20	6	0	1.095004	-1.636114	-0.273041
21	6	0	-1.207763	2.488679	0.885990
22	6	0	-0.400066	2.008297	-0.163482
23	6	0	-0.431328	2.707014	-1.381198
24	1	0	0.222926	2.387266	-2.188503
25	6	0	-2.013923	-0.840801	-1.194310
26	6	0	-1.451463	-0.456675	-2.536779
27	1	0	-2.136714	-0.752704	-3.334863
28	1	0	-1.298849	0.623325	-2.612076
29	1	0	-0.486561	-0.937363	-2.720767
30	6	0	-1.718018	-1.416242	1.158673
31	6	0	-1.202318	-0.945601	-0.058370
32	6	0	-0.831380	-1.667242	2.350629
33	1	0	-1.426935	-1.755661	3.262367
34	1	0	-0.271832	-2.601052	2.225049
35	1	0	-0.097131	-0.872294	2.495753
36	6	0	-3.368365	-1.145787	-1.069666
37	1	0	-4.002712	-1.067400	-1.949037
38	6	0	-3.925140	-1.558256	0.137116
39	6	0	-3.078824	-1.701701	1.234456
40	1	0	-3.486042	-2.054615	2.178703
41	6	0	-1.263116	3.801326	-1.590059
42	1	0	-1.263270	4.310797	-2.549069
43	6	0	-2.079344	4.241996	-0.556187
44	1	0	-2.732561	5.098339	-0.695704
45	6	0	-2.035215	3.592581	0.671221
46	1	0	-2.648870	3.956436	1.491589
47	6	0	-5.399942	-1.840247	0.255248
48	1	0	-5.598762	-2.627833	0.987515
49	1	0	-5.945092	-0.947022	0.581684
50	1	0	-5.824982	-2.148856	-0.703752
51	1	0	4.398419	3.574565	0.474258
52	1	0	1.132867	-5.007524	-0.835806
53	6	0	-1.185994	1.855451	2.254514
54	1	0	-0.184178	1.499788	2.513862
55	1	0	-1.864824	0.998438	2.308933
56	1	0	-1.496935	2.569763	3.022198

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58274558 a.u.

Excited State 1: Singlet-A 3.9815 eV 311.40 nm f=0.2385
<S**2>=0.000
102 ->105 -0.18031
103 ->104 0.65184

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72877500 a.u.

Results

Absorb Energy =	0.165 a.u.	4.479 eV	276.804 nm
Emission Energy =	0.146 a.u.	3.974 eV	312.015 nm
Stokes Shift =	0.019 a.u.	0.505 eV	35.210 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1161.66865675 a.u.
Lowest frequency = 23.1206

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.186126	-0.593959	-0.112457
2	5	0	0.615846	0.761909	-0.068259
3	6	0	2.138017	1.007130	0.028634
4	6	0	2.655973	2.308378	0.158699
5	1	0	1.966307	3.146440	0.152240
6	6	0	4.010926	2.539773	0.296949
7	6	0	4.887202	1.451873	0.310835
8	1	0	5.954658	1.615099	0.425279
9	6	0	4.406687	0.162228	0.182339
10	1	0	5.118274	-0.653962	0.206303
11	6	0	3.029903	-0.085355	0.033846
12	6	0	2.493200	-1.445204	-0.121725
13	6	0	3.342139	-2.560597	-0.222745
14	1	0	4.414614	-2.415625	-0.188709
15	6	0	0.620931	-2.980431	-0.350333
16	1	0	-0.445950	-3.151371	-0.410832
17	6	0	2.862030	-3.845967	-0.377092
18	1	0	3.552474	-4.679462	-0.452357
19	6	0	1.485814	-4.053894	-0.441990
20	6	0	1.098634	-1.669875	-0.187315
21	6	0	-1.094596	2.555186	0.897390

22	6	0	-0.386378	1.984598	-0.176310
23	6	0	-0.490847	2.603088	-1.431408
24	1	0	0.090829	2.214880	-2.264171
25	6	0	-1.999592	-0.900854	-1.210687
26	6	0	-1.404234	-0.603763	-2.561402
27	1	0	-2.040110	-1.006402	-3.353802
28	1	0	-1.310701	0.473064	-2.727602
29	1	0	-0.407161	-1.038836	-2.668207
30	6	0	-1.773206	-1.310842	1.181254
31	6	0	-1.219355	-0.926720	-0.048890
32	6	0	-0.922110	-1.511497	2.408670
33	1	0	-1.530452	-1.459540	3.314973
34	1	0	-0.445424	-2.498143	2.385598
35	1	0	-0.123007	-0.772909	2.486556
36	6	0	-3.359835	-1.187982	-1.104183
37	1	0	-3.969038	-1.167408	-2.004469
38	6	0	-3.953688	-1.510045	0.112567
39	6	0	-3.138687	-1.581553	1.239675
40	1	0	-3.573502	-1.868710	2.193914
41	6	0	-1.303602	3.710321	-1.647772
42	1	0	-1.363421	4.158091	-2.635217
43	6	0	-2.023681	4.243298	-0.585926
44	1	0	-2.660450	5.110824	-0.731757
45	6	0	-1.904717	3.670907	0.674445
46	1	0	-2.445375	4.103763	1.512398
47	6	0	-5.433702	-1.774102	0.208358
48	1	0	-5.660342	-2.495288	0.998557
49	1	0	-5.982480	-0.853967	0.440289
50	1	0	-5.831327	-2.161387	-0.733755
51	1	0	4.391832	3.551237	0.397678
52	1	0	1.084566	-5.054242	-0.569951
53	6	0	-0.997050	1.996216	2.294741
54	1	0	0.010419	1.629786	2.514560
55	1	0	-1.688709	1.159633	2.437005
56	1	0	-1.245692	2.756696	3.040231

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 4.4611 eV 277.92 nm f=0.2443
<S**2>=0.000
102 ->105 0.18934
103 ->104 0.62939

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.74024141 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57550349 a.u.

Excited State 1: Singlet-A 4.4813 eV 276.67 nm f=0.1635
<S**2>=0.000

```
     101 ->105         0.10168
     102 ->105         0.20956
     103 ->104         0.61500
```

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51335728 a.u.
Lowest frequency = 16.7403

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.199923	-0.603443	-0.131316
2	5	0	0.628673	0.815513	-0.053890
3	6	0	2.110789	1.056105	0.060115
4	6	0	2.652490	2.344774	0.192415
5	1	0	1.973751	3.192894	0.184946
6	6	0	4.014270	2.577509	0.340785
7	6	0	4.908659	1.482806	0.366525
8	1	0	5.973421	1.651187	0.490721
9	6	0	4.429429	0.199544	0.233158
10	1	0	5.141683	-0.616444	0.253772
11	6	0	3.033004	-0.070129	0.068528
12	6	0	2.544503	-1.383557	-0.113812
13	6	0	3.394343	-2.533809	-0.166422
14	1	0	4.459576	-2.409072	-0.029585
15	6	0	0.647474	-2.942146	-0.532078
16	1	0	-0.411625	-3.107241	-0.676388
17	6	0	2.904384	-3.799080	-0.402580
18	1	0	3.590777	-4.638942	-0.444097
19	6	0	1.526633	-4.013031	-0.601065
20	6	0	1.100488	-1.635032	-0.264609
21	6	0	-1.204966	2.486551	0.895085
22	6	0	-0.408351	2.004473	-0.162237
23	6	0	-0.458029	2.696694	-1.383153
24	1	0	0.187295	2.376501	-2.197408
25	6	0	-2.005586	-0.854997	-1.200978
26	6	0	-1.435107	-0.484999	-2.544168
27	1	0	-2.122951	-0.774786	-3.342194
28	1	0	-1.265643	0.592027	-2.625338
29	1	0	-0.477061	-0.980984	-2.723671
30	6	0	-1.721070	-1.409733	1.158498
31	6	0	-1.199806	-0.948474	-0.059681
32	6	0	-0.840440	-1.655378	2.356071
33	1	0	-1.438928	-1.723164	3.267591
34	1	0	-0.294312	-2.598892	2.244379
35	1	0	-0.095267	-0.869192	2.491870
36	6	0	-3.360702	-1.159134	-1.080753
37	1	0	-3.990421	-1.089940	-1.964189
38	6	0	-3.923499	-1.560901	0.127235
39	6	0	-3.082511	-1.694611	1.229970
40	1	0	-3.494189	-2.040001	2.175008
41	6	0	-1.297867	3.785990	-1.587118
42	1	0	-1.312585	4.290366	-2.548657
43	6	0	-2.103347	4.228222	-0.545217
44	1	0	-2.762463	5.080583	-0.681020
45	6	0	-2.040693	3.585452	0.685085

46	1	0	-2.645696	3.950751	1.511187
47	6	0	-5.398704	-1.842934	0.240529
48	1	0	-5.599799	-2.628403	0.974379
49	1	0	-5.945274	-0.949079	0.562839
50	1	0	-5.819892	-2.153970	-0.719327
51	1	0	4.388727	3.590920	0.443896
52	1	0	1.149867	-5.009490	-0.804274
53	6	0	-1.163698	1.860358	2.266542
54	1	0	-0.159437	1.502214	2.512455
55	1	0	-1.844350	1.005907	2.336663
56	1	0	-1.460577	2.579595	3.035108

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58432537 a.u.

Excited State 1: Singlet-A 3.9746 eV 311.94 nm f=0.2408
<S**2>=0.000
102 ->105 0.17726
103 ->104 0.65181

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.73000027 a.u.

Results

Absorb Energy =	0.165 a.u.	4.483 eV	276.581 nm
Emission Energy =	0.146 a.u.	3.964 eV	312.774 nm
Stokes Shift =	0.019 a.u.	0.519 eV	36.193 nm

5.1.3 Compound 2 – GS2

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1161.66543182 a.u.
Lowest frequency = 24.5744

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.106847	-0.616642	0.026851
2	5	0	0.621478	0.703906	-0.106643
3	6	0	2.151873	0.838674	-0.266278
4	6	0	2.743731	2.080049	-0.559243
5	1	0	2.105030	2.954204	-0.641738

6	6	0	4.104703	2.206972	-0.755760
7	6	0	4.911793	1.070572	-0.667777
8	1	0	5.983227	1.151065	-0.826247
9	6	0	4.356129	-0.163629	-0.391356
10	1	0	5.012219	-1.024630	-0.351721
11	6	0	2.972223	-0.304360	-0.183899
12	6	0	2.354882	-1.607262	0.102734
13	6	0	3.133009	-2.758629	0.306231
14	1	0	4.212531	-2.679965	0.272823
15	6	0	0.391233	-3.002308	0.438213
16	1	0	-0.684547	-3.102164	0.499957
17	6	0	2.575063	-3.995307	0.561170
18	1	0	3.213114	-4.859512	0.713988
19	6	0	1.188938	-4.114654	0.623895
20	6	0	0.949385	-1.740040	0.179621
21	6	0	-0.290357	2.927619	0.905707
22	6	0	-0.329805	1.966567	-0.125576
23	6	0	-1.204451	2.188761	-1.196455
24	1	0	-1.253930	1.462884	-2.002555
25	6	0	-2.094203	-0.737556	1.130887
26	6	0	-1.486081	-0.351395	2.451884
27	1	0	-2.162849	-0.597969	3.273868
28	1	0	-1.293255	0.725130	2.492594
29	1	0	-0.535440	-0.862850	2.626099
30	6	0	-1.888807	-1.253649	-1.240858
31	6	0	-1.315547	-0.865522	-0.022293
32	6	0	-1.046063	-1.452195	-2.473499
33	1	0	-0.434814	-0.573106	-2.699173
34	1	0	-1.675911	-1.659754	-3.341776
35	1	0	-0.354194	-2.292023	-2.350019
36	6	0	-3.464289	-0.977245	1.037012
37	1	0	-4.073258	-0.880285	1.932483
38	6	0	-4.069309	-1.338619	-0.161899
39	6	0	-3.261276	-1.479470	-1.287755
40	1	0	-3.710664	-1.777536	-2.231875
41	6	0	-2.019760	3.311590	-1.263781
42	1	0	-2.684682	3.451798	-2.110783
43	6	0	-1.982919	4.244354	-0.235555
44	1	0	-2.620388	5.123146	-0.265994
45	6	0	-1.125574	4.044196	0.838494
46	1	0	-1.099515	4.771103	1.646597
47	6	0	-5.557537	-1.556686	-0.245757
48	1	0	-5.808656	-2.320882	-0.986921
49	1	0	-6.074146	-0.635636	-0.539672
50	1	0	-5.970261	-1.868486	0.717714
51	1	0	4.542675	3.173909	-0.983177
52	1	0	0.726838	-5.075894	0.825985
53	6	0	0.649453	2.799204	2.083692
54	1	0	1.634147	3.221044	1.853994
55	1	0	0.258956	3.334289	2.954212
56	1	0	0.813833	1.758892	2.375807

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 4.4470 eV 278.80 nm f=0.2538
<S**2>=0.000
101 ->105 0.10855
102 ->105 -0.18162

103 ->104 0.63229

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73678753 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57263548 a.u.

Excited State 1: Singlet-A 4.4686 eV 277.46 nm f=0.1659
<S**2>=0.000
101 ->105 0.12878
102 ->105 -0.20521
103 ->104 0.61798

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.50761928 a.u.
Lowest frequency = 19.6709

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.113404	-0.647050	0.049324
2	5	0	0.630156	0.742831	-0.108416
3	6	0	2.116700	0.873207	-0.290029
4	6	0	2.731762	2.102061	-0.597692
5	1	0	2.103169	2.982938	-0.692080
6	6	0	4.096574	2.226055	-0.806625
7	6	0	4.923658	1.083981	-0.726050
8	1	0	5.991171	1.167430	-0.900682
9	6	0	4.366858	-0.143955	-0.435361
10	1	0	5.023179	-1.005150	-0.394582
11	6	0	2.970598	-0.300181	-0.206299
12	6	0	2.399983	-1.563656	0.112248
13	6	0	3.180341	-2.739140	0.303011
14	1	0	4.256426	-2.675172	0.216666
15	6	0	0.410558	-2.983243	0.581426
16	1	0	-0.660020	-3.078551	0.701571
17	6	0	2.617231	-3.961737	0.608043
18	1	0	3.258020	-4.826795	0.746029
19	6	0	1.224746	-4.090706	0.752407
20	6	0	0.946354	-1.717948	0.249874
21	6	0	-0.280901	2.995424	0.857996
22	6	0	-0.361157	1.966767	-0.108064
23	6	0	-1.323542	2.099377	-1.121222
24	1	0	-1.409395	1.322705	-1.874935
25	6	0	-2.104783	-0.712735	1.115636
26	6	0	-1.513573	-0.271697	2.426821
27	1	0	-2.240773	-0.383786	3.234697
28	1	0	-1.215807	0.780593	2.388017
29	1	0	-0.624598	-0.854976	2.684859

30	6	0	-1.849204	-1.349858	-1.224916
31	6	0	-1.303436	-0.904837	-0.013651
32	6	0	-0.977447	-1.594278	-2.428759
33	1	0	-0.351636	-0.726868	-2.662216
34	1	0	-1.586986	-1.820905	-3.306635
35	1	0	-0.299462	-2.438434	-2.262477
36	6	0	-3.472670	-0.953138	1.003314
37	1	0	-4.100993	-0.809332	1.878772
38	6	0	-4.052433	-1.372143	-0.190085
39	6	0	-3.221424	-1.571590	-1.290358
40	1	0	-3.652410	-1.910331	-2.229299
41	6	0	-2.169029	3.197474	-1.204010
42	1	0	-2.895102	3.266352	-2.008607
43	6	0	-2.080991	4.199671	-0.246139
44	1	0	-2.739823	5.062133	-0.288299
45	6	0	-1.146218	4.087789	0.774928
46	1	0	-1.085472	4.865726	1.532031
47	6	0	-5.539557	-1.587277	-0.295873
48	1	0	-5.778801	-2.386043	-1.003716
49	1	0	-6.044014	-0.679363	-0.646359
50	1	0	-5.974959	-1.848697	0.672527
51	1	0	4.526595	3.193605	-1.045670
52	1	0	0.785333	-5.050041	1.003107
53	6	0	0.715171	2.956005	1.994845
54	1	0	1.689701	3.352906	1.690644
55	1	0	0.364579	3.558507	2.838087
56	1	0	0.892456	1.938594	2.352870

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58108840 a.u.

Excited State 1: Singlet-A 3.9886 eV 310.84 nm f=0.2291
<S**2>=0.000
102 ->105 -0.18368
103 ->104 0.65181

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72761042 a.u.

Results

Absorb Energy =	0.164 a.u.	4.467 eV	277.568 nm
Emission Energy =	0.147 a.u.	3.987 eV	310.966 nm
Stokes Shift =	0.018 a.u.	0.480 eV	33.398 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran

SCF Done: E(RCAM-B3LYP) = -1161.66883635 a.u.
Lowest frequency = 24.9095

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.112854	-0.617318	0.022585
2	5	0	0.620288	0.705838	-0.109193
3	6	0	2.150733	0.850659	-0.260701
4	6	0	2.737907	2.097768	-0.539796
5	1	0	2.095817	2.969737	-0.618940
6	6	0	4.099791	2.234387	-0.725320
7	6	0	4.913172	1.101840	-0.639242
8	1	0	5.985260	1.189766	-0.788222
9	6	0	4.362705	-0.137884	-0.375411
10	1	0	5.024653	-0.994230	-0.334601
11	6	0	2.977617	-0.288248	-0.179957
12	6	0	2.366143	-1.596928	0.094065
13	6	0	3.150442	-2.746498	0.287176
14	1	0	4.229532	-2.663689	0.252195
15	6	0	0.409247	-3.004223	0.418930
16	1	0	-0.665910	-3.110566	0.480058
17	6	0	2.598264	-3.988021	0.532667
18	1	0	3.240489	-4.850432	0.677470
19	6	0	1.212347	-4.114423	0.595832
20	6	0	0.961004	-1.737090	0.169389
21	6	0	-0.319258	2.921381	0.899427
22	6	0	-0.339824	1.962297	-0.134206
23	6	0	-1.205331	2.179472	-1.214224
24	1	0	-1.238272	1.456570	-2.023876
25	6	0	-2.080593	-0.752458	1.139607
26	6	0	-1.465012	-0.375571	2.460120
27	1	0	-2.135658	-0.631806	3.283977
28	1	0	-1.274749	0.701034	2.510762
29	1	0	-0.511231	-0.884631	2.623602
30	6	0	-1.889187	-1.254784	-1.236826
31	6	0	-1.309217	-0.871722	-0.019744
32	6	0	-1.054458	-1.448374	-2.475759
33	1	0	-0.439917	-0.571104	-2.699136
34	1	0	-1.690316	-1.646955	-3.341548
35	1	0	-0.366726	-2.293022	-2.361708
36	6	0	-3.451333	-0.993463	1.053115
37	1	0	-4.054569	-0.904152	1.953207
38	6	0	-4.063519	-1.348702	-0.144582
39	6	0	-3.262030	-1.482201	-1.276484
40	1	0	-3.716725	-1.776231	-2.219225
41	6	0	-2.031425	3.294540	-1.286768
42	1	0	-2.688519	3.431124	-2.140452
43	6	0	-2.014719	4.224584	-0.254698
44	1	0	-2.660950	5.096777	-0.288754
45	6	0	-1.165376	4.030119	0.827121
46	1	0	-1.154347	4.755068	1.637261
47	6	0	-5.551822	-1.569780	-0.220298
48	1	0	-5.805317	-2.329239	-0.965343
49	1	0	-6.072103	-0.648014	-0.505293
50	1	0	-5.957314	-1.887971	0.744037
51	1	0	4.533808	3.205593	-0.941502
52	1	0	0.754941	-5.079338	0.790546
53	6	0	0.611979	2.801315	2.084996

54	1	0	1.586609	3.253290	1.869590
55	1	0	0.199764	3.314638	2.958444
56	1	0	0.800853	1.761877	2.364735

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 4.4465 eV 278.83 nm f=0.2592
<S**2>=0.000
101 ->105 0.12594
102 ->105 -0.17539
103 ->104 0.63336

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.74046841 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57622765 a.u.

Excited State 1: Singlet-A 4.4693 eV 277.41 nm f=0.1654
<S**2>=0.000
101 ->105 0.14362
102 ->105 -0.19900
103 ->104 0.61825

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51298517 a.u.
Lowest frequency = 19.3298

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.118118	-0.647117	0.044428
2	5	0	0.630022	0.743926	-0.107541
3	6	0	2.117774	0.882537	-0.274344
4	6	0	2.730538	2.115613	-0.562369
5	1	0	2.100507	2.996130	-0.651951
6	6	0	4.097602	2.249213	-0.755866
7	6	0	4.929530	1.108945	-0.675938
8	1	0	5.998978	1.199953	-0.834378
9	6	0	4.376871	-0.123429	-0.405334
10	1	0	5.038360	-0.980299	-0.361292
11	6	0	2.974717	-0.290504	-0.195913
12	6	0	2.409662	-1.558455	0.095241
13	6	0	3.193831	-2.740008	0.258174
14	1	0	4.268561	-2.676653	0.158148
15	6	0	0.422762	-2.986501	0.557141
16	1	0	-0.646849	-3.086172	0.681388

17	6	0	2.632098	-3.964096	0.552662
18	1	0	3.272812	-4.832024	0.671953
19	6	0	1.239990	-4.095192	0.709976
20	6	0	0.954073	-1.718197	0.235619
21	6	0	-0.310806	2.992262	0.846988
22	6	0	-0.367474	1.963650	-0.120266
23	6	0	-1.310531	2.091662	-1.152710
24	1	0	-1.376729	1.315718	-1.909162
25	6	0	-2.089802	-0.725483	1.131220
26	6	0	-1.486291	-0.296881	2.441181
27	1	0	-2.208755	-0.409262	3.253047
28	1	0	-1.180239	0.753219	2.409015
29	1	0	-0.599759	-0.888122	2.689277
30	6	0	-1.856555	-1.345387	-1.216666
31	6	0	-1.299558	-0.907258	-0.007863
32	6	0	-0.997248	-1.585085	-2.430404
33	1	0	-0.377807	-0.715267	-2.671548
34	1	0	-1.615773	-1.814086	-3.301126
35	1	0	-0.314166	-2.426546	-2.271708
36	6	0	-3.458968	-0.966118	1.030881
37	1	0	-4.078421	-0.831090	1.913981
38	6	0	-4.050197	-1.377356	-0.160145
39	6	0	-3.229499	-1.568239	-1.270127
40	1	0	-3.669134	-1.901992	-2.206734
41	6	0	-2.161027	3.184962	-1.251229
42	1	0	-2.871407	3.250668	-2.069956
43	6	0	-2.097730	4.186992	-0.290188
44	1	0	-2.761073	5.045265	-0.344097
45	6	0	-1.181849	4.079721	0.748554
46	1	0	-1.140146	4.857340	1.507212
47	6	0	-5.537856	-1.595273	-0.252572
48	1	0	-5.781460	-2.392166	-0.960882
49	1	0	-6.047081	-0.687472	-0.596309
50	1	0	-5.963263	-1.859457	0.719396
51	1	0	4.525569	3.221331	-0.979365
52	1	0	0.803861	-5.057982	0.953153
53	6	0	0.666287	2.962486	2.000570
54	1	0	1.628070	3.407415	1.722698
55	1	0	0.278198	3.529740	2.851665
56	1	0	0.878155	1.944518	2.336658

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58507884 a.u.

Excited State 1: Singlet-A 3.9691 eV 312.38 nm f=0.2341
<S**2>=0.000
102 ->105 -0.17709
103 ->104 0.65299

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.73063188 a.u.

Results

Absorb Energy =	0.164 a.u.	4.469 eV	277.418 nm
Emission Energy =	0.146 a.u.	3.961 eV	313.036 nm
Stokes Shift =	0.019 a.u.	0.509 eV	35.618 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1161.67029167 a.u.
Lowest frequency = 24.8695

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.115798	-0.617081	0.020626
2	5	0	0.619862	0.707303	-0.110683
3	6	0	2.150224	0.856785	-0.258749
4	6	0	2.735035	2.106447	-0.532012
5	1	0	2.091318	2.977348	-0.609602
6	6	0	4.097226	2.247391	-0.713002
7	6	0	4.913515	1.116651	-0.627955
8	1	0	5.985784	1.207954	-0.773106
9	6	0	4.365634	-0.125505	-0.369317
10	1	0	5.030196	-0.979756	-0.328111
11	6	0	2.980186	-0.280143	-0.178664
12	6	0	2.371659	-1.591336	0.090535
13	6	0	3.159022	-2.739728	0.279642
14	1	0	4.237889	-2.654781	0.243874
15	6	0	0.418151	-3.004305	0.411763
16	1	0	-0.656672	-3.113789	0.472801
17	6	0	2.609731	-3.983340	0.521763
18	1	0	3.254018	-4.844676	0.663482
19	6	0	1.223982	-4.113194	0.585365
20	6	0	0.966785	-1.735103	0.165407
21	6	0	-0.333558	2.917925	0.897527
22	6	0	-0.344495	1.960892	-0.138157
23	6	0	-1.205567	2.176552	-1.222429
24	1	0	-1.229724	1.456263	-2.034765
25	6	0	-2.074372	-0.760080	1.142885
26	6	0	-1.455991	-0.387287	2.463385
27	1	0	-2.124645	-0.646913	3.287711
28	1	0	-1.265774	0.689140	2.518267
29	1	0	-0.501423	-0.896093	2.622899
30	6	0	-1.888397	-1.255985	-1.235623
31	6	0	-1.305894	-0.874700	-0.019084
32	6	0	-1.056842	-1.447314	-2.477061
33	1	0	-0.439342	-0.571601	-2.698085
34	1	0	-1.695091	-1.640056	-3.342317
35	1	0	-0.372489	-2.295379	-2.367655
36	6	0	-3.445321	-1.002158	1.059276
37	1	0	-4.046217	-0.916894	1.961300
38	6	0	-4.060279	-1.354453	-0.138142
39	6	0	-3.261342	-1.484301	-1.272502
40	1	0	-3.718067	-1.776560	-2.214757

41	6	0	-2.037985	3.287059	-1.296016
42	1	0	-2.691190	3.422622	-2.152838
43	6	0	-2.031980	4.214241	-0.260847
44	1	0	-2.683251	5.082619	-0.295476
45	6	0	-1.186073	4.022058	0.824199
46	1	0	-1.182685	4.745122	1.636032
47	6	0	-5.548513	-1.577207	-0.210890
48	1	0	-5.802128	-2.338925	-0.953518
49	1	0	-6.070098	-0.656883	-0.498179
50	1	0	-5.952085	-1.892580	0.755108
51	1	0	4.529352	3.220455	-0.924364
52	1	0	0.768946	-5.079704	0.777481
53	6	0	0.594209	2.801829	2.086159
54	1	0	1.562631	3.270278	1.877770
55	1	0	0.171321	3.302567	2.961738
56	1	0	0.797031	1.763140	2.358618

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 4.4513 eV 278.54 nm f=0.2458
<S**2>=0.000
101 ->105 0.12984
102 ->105 -0.17859
103 ->104 0.63163

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.74205054 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57768798 a.u.

Excited State 1: Singlet-A 4.4711 eV 277.30 nm f=0.1649
<S**2>=0.000
101 ->105 0.14511
102 ->105 -0.19909
103 ->104 0.61827

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51531248 a.u.
Lowest frequency = 20.7834

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.121631	-0.647125	0.041469
2	5	0	0.628900	0.745122	-0.107751

3	6	0	2.117115	0.889801	-0.267694
4	6	0	2.726847	2.125739	-0.546714
5	1	0	2.094900	3.005204	-0.633658
6	6	0	4.094695	2.265477	-0.733453
7	6	0	4.930489	1.127293	-0.654408
8	1	0	6.000532	1.223340	-0.805655
9	6	0	4.381662	-0.107939	-0.392950
10	1	0	5.046601	-0.961960	-0.347645
11	6	0	2.977309	-0.281797	-0.191987
12	6	0	2.416730	-1.552349	0.087230
13	6	0	3.204477	-2.735046	0.238024
14	1	0	4.278388	-2.670152	0.131174
15	6	0	0.433623	-2.986896	0.547671
16	1	0	-0.635371	-3.090179	0.674095
17	6	0	2.645655	-3.960435	0.529395
18	1	0	3.287787	-4.828350	0.640883
19	6	0	1.254083	-4.094615	0.693330
20	6	0	0.960684	-1.716892	0.229207
21	6	0	-0.329783	2.989252	0.841829
22	6	0	-0.373740	1.961053	-0.126277
23	6	0	-1.308701	2.085510	-1.166959
24	1	0	-1.364282	1.310428	-1.925175
25	6	0	-2.080988	-0.733669	1.137737
26	6	0	-1.471739	-0.310336	2.446912
27	1	0	-2.191676	-0.423274	3.260855
28	1	0	-1.161916	0.738760	2.417860
29	1	0	-0.586076	-0.904930	2.690015
30	6	0	-1.857622	-1.346689	-1.213122
31	6	0	-1.295836	-0.910493	-0.005759
32	6	0	-1.003825	-1.583967	-2.431232
33	1	0	-0.385984	-0.713607	-2.674348
34	1	0	-1.626247	-1.812159	-3.299295
35	1	0	-0.319705	-2.425349	-2.276715
36	6	0	-3.450625	-0.975108	1.042981
37	1	0	-4.066069	-0.844296	1.929491
38	6	0	-4.046810	-1.383686	-0.146760
39	6	0	-3.230709	-1.570897	-1.260975
40	1	0	-3.674136	-1.903162	-2.196258
41	6	0	-2.164337	3.174371	-1.271367
42	1	0	-2.867960	3.237496	-2.096095
43	6	0	-2.114119	4.175980	-0.308565
44	1	0	-2.781488	5.030775	-0.367046
45	6	0	-1.206055	4.072442	0.737400
46	1	0	-1.174267	4.849657	1.496913
47	6	0	-5.534560	-1.603586	-0.233290
48	1	0	-5.779475	-2.401230	-0.940223
49	1	0	-6.046241	-0.696860	-0.576228
50	1	0	-5.955794	-1.867160	0.740601
51	1	0	4.520276	3.240255	-0.949680
52	1	0	0.821057	-5.059336	0.934435
53	6	0	0.638843	2.965901	2.002696
54	1	0	1.588545	3.445097	1.740240
55	1	0	0.228248	3.506098	2.860767
56	1	0	0.877863	1.948657	2.321764

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58676155 a.u.

```
 Excited State   1:      Singlet-A      3.9609 eV  313.02 nm  f=0.2359
<S**2>=0.000
     102 ->105         0.17529
     103 ->104         0.65339

Step7

  Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

 SCF Done: E(RCAM-B3LYP) = -1161.73189527 a.u.

                              Results
 ------------------------------------------------------------------
     Absorb Energy     =  | 0.164 a.u. | 4.473 eV | 277.212 nm
 -------------------------|------------|----------|----------------
     Emission Energy   =  | 0.145 a.u. | 3.949 eV | 313.940 nm
 -------------------------|------------|----------|----------------
     Stokes Shift      =  | 0.019 a.u. | 0.523 eV | 36.728 nm
 ------------------------------------------------------------------
```

5.1.4 Compound 3 – GS1

<u>*n*-hexane</u>

```
Step1

 Method: cam-b3lyp/6-31G(d)
 Solvent : n-Hexane
 SCF Done: E(RCAM-B3LYP) = -1161.66406680 a.u.
 Lowest frequency =  25.7299

                       Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          7           0        0.712768    0.637126   -0.160359
      2          5           0        0.041342   -0.612297   -0.021315
      3          6           0        0.934756   -1.860592    0.147898
      4          6           0        0.369111   -3.121024    0.407239
      5          1           0       -0.712928   -3.207627    0.438212
      6          6           0        1.154994   -4.235202    0.629555
      7          6           0        2.544704   -4.101484    0.602653
      8          1           0        3.177299   -4.964926    0.786764
      9          6           0        3.127117   -2.874603    0.346277
     10          1           0        4.208468   -2.809063    0.345444
     11          6           0        2.337974   -1.736598    0.104844
     12          6           0        2.927567   -0.425556   -0.203531
     13          6           0        4.308935   -0.273390   -0.406651
     14          1           0        4.952446   -1.141367   -0.333964
     15          6           0        2.704175    1.952077   -0.659426
     16          1           0        2.076582    2.825623   -0.780378
     17          6           0        4.883045    0.942940   -0.717163
     18          1           0        5.955000    1.016546   -0.868110
     19          6           0        4.068045    2.064900   -0.846706
     20          6           0        2.113120    0.722604   -0.329258
     21          6           0       -2.166106   -1.089269   -1.258138
     22          6           0       -1.535432   -0.728448   -0.050655
     23          6           0       -2.330849   -0.561962    1.094025
```

24	6	0	0.037848	2.697070	1.013706
25	6	0	-0.026718	1.874421	-0.121415
26	6	0	0.917225	2.366291	2.190507
27	1	0	0.905633	1.298539	2.420322
28	1	0	0.593439	2.913625	3.079412
29	1	0	1.959487	2.638370	1.991144
30	6	0	-1.559892	3.404858	-1.188722
31	1	0	-2.173938	3.670571	-2.043148
32	6	0	-0.721303	3.867910	1.014289
33	1	0	-0.686170	4.510605	1.889651
34	6	0	-3.714181	-0.720849	1.014187
35	1	0	-4.312656	-0.591915	1.913602
36	6	0	-4.346049	-1.043004	-0.181251
37	6	0	-3.549867	-1.231081	-1.308504
38	1	0	-4.019289	-1.506193	-2.250712
39	1	0	0.701317	-5.200899	0.829786
40	1	0	4.494314	3.029392	-1.104351
41	6	0	-1.354774	-1.364819	-2.503004
42	1	0	-0.757888	-2.276978	-2.391871
43	1	0	-2.000996	-1.494755	-3.375286
44	1	0	-0.650410	-0.556832	-2.727618
45	6	0	-5.844946	-1.174368	-0.260465
46	1	0	-6.141799	-1.948261	-0.974682
47	1	0	-6.275624	-1.427175	0.712584
48	1	0	-6.307889	-0.236068	-0.588337
49	6	0	-1.714803	-0.202486	2.423965
50	1	0	-0.759459	-0.713757	2.581038
51	1	0	-1.526746	0.874445	2.492359
52	1	0	-2.376627	-0.472059	3.251946
53	6	0	-1.515165	4.224644	-0.068595
54	1	0	-2.096602	5.140722	-0.035366
55	6	0	-0.812804	2.234552	-1.210747
56	1	0	-0.835428	1.585863	-2.078835

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 4.4581 eV 278.11 nm f=0.2538
<S**2>=0.000
100 ->105 0.19653
103 ->104 0.62362

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73525324 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57065850 a.u.

Excited State 1: Singlet-A 4.4804 eV 276.72 nm f=0.1659
<S**2>=0.000
100 ->105 0.21227
103 ->104 0.60956

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.50622183 a.u.
Lowest frequency = 20.4570

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.708174	0.633961	-0.188320
2	5	0	0.015721	-0.673382	-0.019629
3	6	0	0.907305	-1.868003	0.185619
4	6	0	0.386635	-3.146151	0.454618
5	1	0	-0.693312	-3.264459	0.485016
6	6	0	1.195316	-4.246240	0.697417
7	6	0	2.599618	-4.093675	0.678838
8	1	0	3.242631	-4.945855	0.874396
9	6	0	3.157674	-2.863331	0.408650
10	1	0	4.238314	-2.782966	0.389562
11	6	0	2.351344	-1.716804	0.147097
12	6	0	2.915929	-0.461430	-0.196121
13	6	0	4.317768	-0.236934	-0.317057
14	1	0	5.002448	-1.039356	-0.076988
15	6	0	2.620711	1.896267	-0.947404
16	1	0	1.960219	2.715418	-1.200892
17	6	0	4.837070	0.964457	-0.753596
18	1	0	5.912681	1.077156	-0.847439
19	6	0	3.990719	2.036836	-1.096644
20	6	0	2.055883	0.702513	-0.452859
21	6	0	-2.204313	-1.149112	-1.256508
22	6	0	-1.558396	-0.756161	-0.067021
23	6	0	-2.344769	-0.515113	1.072747
24	6	0	0.189821	2.728020	0.990082
25	6	0	-0.020467	1.867304	-0.101726
26	6	0	1.186673	2.414310	2.073739
27	1	0	1.150490	1.360576	2.363329
28	1	0	0.990303	3.020461	2.961439
29	1	0	2.210517	2.622054	1.744710
30	6	0	-1.686708	3.361953	-1.007777
31	1	0	-2.409068	3.599658	-1.781914
32	6	0	-0.562770	3.900022	1.047623
33	1	0	-0.418420	4.569534	1.890950
34	6	0	-3.731038	-0.648815	1.006787
35	1	0	-4.321836	-0.468143	1.902380
36	6	0	-4.375931	-1.011884	-0.170295
37	6	0	-3.591083	-1.263869	-1.293207
38	1	0	-4.072609	-1.567133	-2.220516
39	1	0	0.754801	-5.215272	0.908884
40	1	0	4.404522	2.965817	-1.472621
41	6	0	-1.405983	-1.464786	-2.499861
42	1	0	-0.745150	-2.322887	-2.340322
43	1	0	-2.062751	-1.696113	-3.342995
44	1	0	-0.763927	-0.628374	-2.799823
45	6	0	-5.877514	-1.117285	-0.235504
46	1	0	-6.193629	-1.914260	-0.915194
47	1	0	-6.306724	-1.320932	0.749628
48	1	0	-6.324592	-0.184609	-0.599619
49	6	0	-1.709782	-0.106747	2.379897

50	1	0	-0.772841	-0.644806	2.556646
51	1	0	-1.480399	0.964862	2.389033
52	1	0	-2.376506	-0.305944	3.223755
53	6	0	-1.490724	4.223361	0.063966
54	1	0	-2.061560	5.143454	0.139784
55	6	0	-0.953511	2.185726	-1.086178
56	1	0	-1.096301	1.504717	-1.916741

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1) SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.57968924 a.u.

Excited State 1: Singlet-A 3.9434 eV 314.41 nm f=0.2344 <S**2>=0.000

101 ->105	-0.13631
102 ->105	0.11889
103 ->104	0.65565

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72454077 a.u.

Results

Absorb Energy =	0.165 a.u.	4.479 eV	276.821 nm
Emission Energy =	0.145 a.u.	3.942 eV	314.552 nm
Stokes Shift =	0.020 a.u.	0.537 eV	37.731 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1161.66749554 a.u.
Lowest frequency = 24.8351

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.713180	0.638893	-0.158735
2	5	0	0.045980	-0.612531	-0.021230
3	6	0	0.943140	-1.859217	0.142444
4	6	0	0.381795	-3.123742	0.392730
5	1	0	-0.699853	-3.214714	0.424084
6	6	0	1.170947	-4.237857	0.605181
7	6	0	2.560677	-4.100159	0.576576
8	1	0	3.195972	-4.963309	0.751775
9	6	0	3.139351	-2.869289	0.329119
10	1	0	4.220484	-2.802040	0.325317
11	6	0	2.346293	-1.731029	0.099045

12	6	0	2.932429	-0.415450	-0.197569
13	6	0	4.314976	-0.256827	-0.391032
14	1	0	4.962498	-1.121761	-0.318442
15	6	0	2.702511	1.964728	-0.638158
16	1	0	2.073387	2.837600	-0.755264
17	6	0	4.886073	0.964139	-0.690212
18	1	0	5.958626	1.042989	-0.833609
19	6	0	4.067229	2.084134	-0.817012
20	6	0	2.113917	0.730583	-0.320130
21	6	0	-2.165409	-1.089652	-1.254700
22	6	0	-1.531135	-0.733008	-0.047454
23	6	0	-2.323389	-0.574011	1.101044
24	6	0	0.011945	2.694707	1.009251
25	6	0	-0.032637	1.873181	-0.127534
26	6	0	0.881085	2.372064	2.195934
27	1	0	0.893102	1.302106	2.414610
28	1	0	0.531367	2.902231	3.085240
29	1	0	1.918603	2.673546	2.014350
30	6	0	-1.558783	3.396816	-1.215644
31	1	0	-2.160248	3.661520	-2.079269
32	6	0	-0.755824	3.860489	1.001390
33	1	0	-0.737299	4.501935	1.878053
34	6	0	-3.707350	-0.734576	1.024943
35	1	0	-4.302944	-0.611870	1.927135
36	6	0	-4.342989	-1.051416	-0.170521
37	6	0	-3.549634	-1.233058	-1.301455
38	1	0	-4.021577	-1.504253	-2.243485
39	1	0	0.720334	-5.206366	0.798285
40	1	0	4.491229	3.052135	-1.064701
41	6	0	-1.358312	-1.360482	-2.503361
42	1	0	-0.769858	-2.279228	-2.400864
43	1	0	-2.006875	-1.477229	-3.375621
44	1	0	-0.647406	-0.556790	-2.721568
45	6	0	-5.842049	-1.184882	-0.245640
46	1	0	-6.139588	-1.954416	-0.964133
47	1	0	-6.268995	-1.443508	0.727440
48	1	0	-6.307248	-0.245375	-0.566661
49	6	0	-1.704752	-0.221536	2.431895
50	1	0	-0.743231	-0.723698	2.579624
51	1	0	-1.526706	0.856323	2.511073
52	1	0	-2.360320	-0.505635	3.259883
53	6	0	-1.536503	4.214181	-0.092367
54	1	0	-2.124167	5.126433	-0.065850
55	6	0	-0.804138	2.230887	-1.228534
56	1	0	-0.808241	1.585477	-2.099472

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 4.4583 eV 278.10 nm f=0.2585
<S**2>=0.000
101 ->105 -0.19466
103 ->104 0.62654

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73894230 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57422596 a.u.

Excited State 1: Singlet-A 4.4819 eV 276.64 nm f=0.1650
<S**2>=0.000
101 ->105 0.22287
103 ->104 0.61160

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51162367 a.u.
Lowest frequency = 21.4217

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.707914	0.637358	-0.184995
2	5	0	0.022464	-0.671900	-0.021830
3	6	0	0.919690	-1.865749	0.172395
4	6	0	0.406292	-3.147613	0.426408
5	1	0	-0.673074	-3.272957	0.453757
6	6	0	1.219712	-4.248783	0.657888
7	6	0	2.624227	-4.089242	0.642335
8	1	0	3.270654	-4.941147	0.827645
9	6	0	3.177145	-2.854637	0.388590
10	1	0	4.257333	-2.769704	0.372111
11	6	0	2.363986	-1.705095	0.138635
12	6	0	2.923696	-0.447063	-0.183593
13	6	0	4.329603	-0.213147	-0.288064
14	1	0	5.016965	-1.012121	-0.044932
15	6	0	2.620332	1.915267	-0.918950
16	1	0	1.959640	2.735451	-1.167977
17	6	0	4.842553	0.992406	-0.713822
18	1	0	5.918012	1.114250	-0.797444
19	6	0	3.991337	2.062508	-1.058008
20	6	0	2.057880	0.716477	-0.438567
21	6	0	-2.202429	-1.149846	-1.251255
22	6	0	-1.551948	-0.762099	-0.062305
23	6	0	-2.333470	-0.533157	1.083598
24	6	0	0.147527	2.725705	0.986890
25	6	0	-0.031898	1.866340	-0.110975
26	6	0	1.128353	2.422301	2.087936
27	1	0	1.107152	1.366374	2.370316
28	1	0	0.904704	3.019294	2.975198
29	1	0	2.153732	2.652064	1.778712
30	6	0	-1.687040	3.351354	-1.053340
31	1	0	-2.390819	3.587207	-1.844955
32	6	0	-0.616780	3.891405	1.030817
33	1	0	-0.496907	4.560076	1.878521
34	6	0	-3.720105	-0.672241	1.024039
35	1	0	-4.306823	-0.500807	1.924110
36	6	0	-4.369971	-1.029239	-0.152710
37	6	0	-3.589373	-1.269901	-1.281667

38	1	0	-4.074371	-1.567911	-2.208809
39	1	0	0.782924	-5.221997	0.857523
40	1	0	4.403559	2.996367	-1.423710
41	6	0	-1.410132	-1.458508	-2.500295
42	1	0	-0.774550	-2.338863	-2.359161
43	1	0	-2.071154	-1.653119	-3.349198
44	1	0	-0.744452	-0.634098	-2.779908
45	6	0	-5.871538	-1.140489	-0.211129
46	1	0	-6.187434	-1.934487	-0.894268
47	1	0	-6.294932	-1.350488	0.775101
48	1	0	-6.323626	-0.207621	-0.568295
49	6	0	-1.694758	-0.130940	2.391039
50	1	0	-0.748390	-0.656193	2.555192
51	1	0	-1.480461	0.943513	2.411587
52	1	0	-2.352402	-0.349316	3.237158
53	6	0	-1.524508	4.210117	0.026760
54	1	0	-2.104409	5.125283	0.091952
55	6	0	-0.942067	2.181310	-1.117662
56	1	0	-1.056468	1.504294	-1.956045

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58357140 a.u.

Excited State 1: Singlet-A 3.9279 eV 315.65 nm f=0.2401
<S**2>=0.000
101 ->105 -0.12340
102 ->105 0.12636
103 ->104 0.65623

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72760348 a.u.

Results

Absorb Energy =	0.165 a.u.	4.482 eV	276.617 nm
Emission Energy =	0.144 a.u.	3.919 eV	316.342 nm
Stokes Shift =	0.021 a.u.	0.563 eV	39.725 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1161.66897293 a.u.
Lowest frequency = 24.5386

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	7	0	0.712053	0.640310	-0.158460
2	5	0	0.049805	-0.613685	-0.022057
3	6	0	0.951290	-1.857713	0.138038
4	6	0	0.394584	-3.125470	0.383094
5	1	0	-0.686684	-3.220770	0.414476
6	6	0	1.187660	-4.237924	0.590221
7	6	0	2.577066	-4.095323	0.561041
8	1	0	3.215434	-4.957056	0.731587
9	6	0	3.151392	-2.861248	0.318621
10	1	0	4.232270	-2.790812	0.313635
11	6	0	2.354097	-1.724483	0.094630
12	6	0	2.935730	-0.405274	-0.195254
13	6	0	4.318496	-0.240540	-0.383476
14	1	0	4.969556	-1.102850	-0.311732
15	6	0	2.697878	1.976108	-0.625773
16	1	0	2.066315	2.847515	-0.740221
17	6	0	4.885712	0.984113	-0.675522
18	1	0	5.958396	1.067817	-0.814847
19	6	0	4.062807	2.101611	-0.799807
20	6	0	2.112934	0.738147	-0.315512
21	6	0	-2.163686	-1.090004	-1.254055
22	6	0	-1.527179	-0.739027	-0.046060
23	6	0	-2.317316	-0.587852	1.105188
24	6	0	-0.007655	2.690762	1.008611
25	6	0	-0.039369	1.871588	-0.130218
26	6	0	0.855982	2.372269	2.200448
27	1	0	0.884880	1.300922	2.410085
28	1	0	0.489551	2.888765	3.090998
29	1	0	1.889355	2.694226	2.030363
30	6	0	-1.563623	3.390839	-1.227856
31	1	0	-2.158144	3.655496	-2.096291
32	6	0	-0.781841	3.852576	0.997541
33	1	0	-0.773514	4.492042	1.875742
34	6	0	-3.701661	-0.748889	1.030965
35	1	0	-4.295430	-0.632359	1.935165
36	6	0	-4.339641	-1.058753	-0.165323
37	6	0	-3.548142	-1.233753	-1.298943
38	1	0	-4.021753	-1.500121	-2.241468
39	1	0	0.740577	-5.208824	0.779298
40	1	0	4.483831	3.072442	-1.041215
41	6	0	-1.359074	-1.355719	-2.505421
42	1	0	-0.775684	-2.278484	-2.409715
43	1	0	-2.008935	-1.463067	-3.377846
44	1	0	-0.644198	-0.554332	-2.718484
45	6	0	-5.838811	-1.192621	-0.238433
46	1	0	-6.137024	-1.960201	-0.958672
47	1	0	-6.264098	-1.453503	0.734724
48	1	0	-6.304736	-0.252523	-0.556628
49	6	0	-1.696921	-0.243156	2.437420
50	1	0	-0.730535	-0.738115	2.576957
51	1	0	-1.527493	0.835271	2.527367
52	1	0	-2.347314	-0.540792	3.264682
53	6	0	-1.555315	4.205156	-0.101808
54	1	0	-2.147649	5.114418	-0.077910
55	6	0	-0.802887	2.228695	-1.237341
56	1	0	-0.795402	1.586469	-2.110651

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 4.4636 eV 277.77 nm f=0.2447
<S**2>=0.000
101 ->105 0.20202
103 ->104 0.62560

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.74054373 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57568902 a.u.

Excited State 1: Singlet-A 4.4840 eV 276.50 nm f=0.1642
<S**2>=0.000
101 ->105 0.22407
103 ->104 0.61226

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51395547 a.u.
Lowest frequency = 21.4669

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.706077	0.640024	-0.183659
2	5	0	0.027984	-0.671712	-0.022583
3	6	0	0.931022	-1.862915	0.166005
4	6	0	0.424514	-3.147912	0.412400
5	1	0	-0.654174	-3.279592	0.438387
6	6	0	1.243370	-4.247389	0.637835
7	6	0	2.647453	-4.080817	0.623630
8	1	0	3.297757	-4.930834	0.803883
9	6	0	3.194646	-2.842685	0.377795
10	1	0	4.274367	-2.752743	0.362623
11	6	0	2.375149	-1.694015	0.133689
12	6	0	2.928715	-0.433105	-0.178826
13	6	0	4.335707	-0.191307	-0.277102
14	1	0	5.026338	-0.987570	-0.034689
15	6	0	2.615127	1.931401	-0.903208
16	1	0	1.952236	2.750873	-1.148445
17	6	0	4.842584	1.017976	-0.696406
18	1	0	5.917529	1.146654	-0.776121
19	6	0	3.986197	2.085453	-1.038401
20	6	0	2.057101	0.728228	-0.431369
21	6	0	-2.197674	-1.151100	-1.250196
22	6	0	-1.546273	-0.769450	-0.059630
23	6	0	-2.326491	-0.551197	1.089328
24	6	0	0.117390	2.720750	0.988725

25	6	0	-0.042430	1.864804	-0.114541
26	6	0	1.089613	2.422196	2.098706
27	1	0	1.078395	1.364623	2.375084
28	1	0	0.849962	3.011698	2.986714
29	1	0	2.115132	2.666380	1.801076
30	6	0	-1.694015	3.343421	-1.073539
31	1	0	-2.387464	3.578980	-1.874307
32	6	0	-0.656049	3.880936	1.027925
33	1	0	-0.551639	4.546984	1.879663
34	6	0	-3.713191	-0.693406	1.031106
35	1	0	-4.298815	-0.530007	1.933368
36	6	0	-4.364205	-1.043384	-0.147356
37	6	0	-3.584567	-1.274320	-1.279305
38	1	0	-4.070291	-1.566820	-2.207782
39	1	0	0.811052	-5.223780	0.831537
40	1	0	4.394869	3.023321	-1.397870
41	6	0	-1.406817	-1.452440	-2.501979
42	1	0	-0.790131	-2.348376	-2.374577
43	1	0	-2.068271	-1.618848	-3.356438
44	1	0	-0.723565	-0.636991	-2.764127
45	6	0	-5.865637	-1.157671	-0.204450
46	1	0	-6.180482	-1.948749	-0.891383
47	1	0	-6.287287	-1.373033	0.781322
48	1	0	-6.320020	-0.224095	-0.556756
49	6	0	-1.687488	-0.155808	2.398836
50	1	0	-0.734587	-0.671689	2.554325
51	1	0	-1.484830	0.920628	2.430588
52	1	0	-2.339687	-0.390266	3.244811
53	6	0	-1.552781	4.197733	0.013371
54	1	0	-2.139873	5.108520	0.074917
55	6	0	-0.939742	2.178854	-1.133051
56	1	0	-1.036355	1.506119	-1.977219

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58518290 a.u.

Excited State 1: Singlet-A 3.9235 eV 316.01 nm f=0.2426
<S**2>=0.000
101 ->105 -0.11532
102 ->105 0.13196
103 ->104 0.65622

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72894310 a.u.

Results

Absorb Energy =	0.165 a.u.	4.486 eV	276.385 nm
Emission Energy =	0.144 a.u.	3.912 eV	316.940 nm
Stokes Shift =	0.021 a.u.	0.574 eV	40.555 nm

5.1.5 Compound 3 – GS2

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1161.66212970 a.u.
Lowest frequency = 20.5222

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.718853	0.680735	-0.055357
2	5	0	0.115199	-0.609210	-0.104495
3	6	0	1.071965	-1.818872	-0.180018
4	6	0	0.570280	-3.124169	-0.324027
5	1	0	-0.505929	-3.265663	-0.354811
6	6	0	1.409785	-4.215322	-0.433449
7	6	0	2.791318	-4.013144	-0.405311
8	1	0	3.466382	-4.859063	-0.496682
9	6	0	3.311533	-2.740561	-0.267287
10	1	0	4.388507	-2.624922	-0.261896
11	6	0	2.466751	-1.622639	-0.147968
12	6	0	2.991254	-0.257741	0.006402
13	6	0	4.368614	-0.013626	0.131372
14	1	0	5.056515	-0.849819	0.124729
15	6	0	2.656897	2.144441	0.182040
16	1	0	1.992777	2.997676	0.207812
17	6	0	4.887322	1.257652	0.273339
18	1	0	5.958637	1.401343	0.368138
19	6	0	4.018594	2.345380	0.298098
20	6	0	2.119322	0.855437	0.036478
21	6	0	-2.060310	-1.209774	1.147008
22	6	0	-1.454700	-0.802708	-0.060790
23	6	0	-2.269418	-0.654497	-1.195056
24	6	0	-0.074138	1.883112	-0.176306
25	6	0	-1.399138	3.660769	0.728627
26	1	0	-1.860350	4.143573	1.585748
27	6	0	-0.940287	3.612692	-1.628183
28	1	0	-1.034539	4.042581	-2.620323
29	6	0	-3.648846	-0.839182	-1.096002
30	1	0	-4.261423	-0.720557	-1.987685
31	6	0	-4.258463	-1.176660	0.105807
32	6	0	-3.441016	-1.371692	1.216759
33	1	0	-3.890681	-1.673888	2.160503
34	1	0	1.004572	-5.216271	-0.544992
35	1	0	4.401441	3.354646	0.412804
36	6	0	-1.234112	-1.556658	2.365955
37	1	0	-0.903765	-2.601007	2.322816
38	1	0	-1.814982	-1.435269	3.285096
39	1	0	-0.332886	-0.946145	2.455089
40	6	0	-5.754190	-1.325941	0.207947
41	1	0	-6.030854	-2.107180	0.922246
42	1	0	-6.197424	-1.577787	-0.759696
43	1	0	-6.222026	-0.394706	0.548716
44	6	0	-1.695159	-0.321415	-2.552010

45	1	0	-0.616463	-0.494161	-2.597219
46	1	0	-1.873388	0.726454	-2.814183
47	1	0	-2.160703	-0.935437	-3.329540
48	6	0	-1.549749	4.216044	-0.534312
49	1	0	-2.130918	5.124063	-0.661392
50	6	0	-0.658158	2.495153	0.937671
51	6	0	-0.508321	1.943751	2.328627
52	1	0	0.468622	1.477507	2.477732
53	1	0	-1.271911	1.186912	2.531359
54	1	0	-0.624930	2.737938	3.070695
55	6	0	-0.202043	2.452776	-1.441402
56	1	0	0.294239	1.974445	-2.279127

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 4.4690 eV 277.43 nm f=0.2565
<S**2>=0.000

100 ->104	-0.10334
100 ->105	0.19321
103 ->104	0.62330
103 ->105	0.10927

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73335054 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.56833074 a.u.

Excited State 1: Singlet-A 4.4919 eV 276.02 nm f=0.1669
<S**2>=0.000

100 ->104	-0.11481
100 ->105	0.21413
103 ->104	0.60762
103 ->105	0.11495

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.50343048 a.u.
Lowest frequency = 17.0418

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.735407	0.703416	-0.010647
2	5	0	0.117605	-0.646236	-0.109533
3	6	0	1.072968	-1.801863	-0.231888
4	6	0	0.623302	-3.122415	-0.405087
5	1	0	-0.448307	-3.299222	-0.441720

6	6	0	1.490149	-4.196875	-0.545355
7	6	0	2.884456	-3.972825	-0.520795
8	1	0	3.572869	-4.803115	-0.640610
9	6	0	3.374291	-2.696124	-0.346391
10	1	0	4.448963	-2.558559	-0.331786
11	6	0	2.507450	-1.574630	-0.188867
12	6	0	3.006143	-0.264668	0.033379
13	6	0	4.396463	0.028228	0.147199
14	1	0	5.112814	-0.776212	0.051094
15	6	0	2.612350	2.164174	0.418263
16	1	0	1.927474	2.992685	0.533401
17	6	0	4.867313	1.303009	0.387009
18	1	0	5.936499	1.470492	0.471152
19	6	0	3.976676	2.381387	0.534285
20	6	0	2.090816	0.880745	0.149075
21	6	0	-2.049370	-1.298378	1.138938
22	6	0	-1.450332	-0.824680	-0.049329
23	6	0	-2.276133	-0.608811	-1.166530
24	6	0	-0.061243	1.894601	-0.177295
25	6	0	-1.533450	3.606316	0.615168
26	1	0	-2.107054	4.049112	1.424621
27	6	0	-0.786789	3.654168	-1.668110
28	1	0	-0.772060	4.116293	-2.649970
29	6	0	-3.654596	-0.800477	-1.068659
30	1	0	-4.273378	-0.632636	-1.948045
31	6	0	-4.255185	-1.208788	0.115543
32	6	0	-3.429606	-1.465862	1.208006
33	1	0	-3.873040	-1.821119	2.136014
34	1	0	1.101346	-5.200615	-0.683834
35	1	0	4.349694	3.378718	0.739420
36	6	0	-1.216371	-1.693363	2.338005
37	1	0	-0.805433	-2.701140	2.210824
38	1	0	-1.818778	-1.695608	3.251359
39	1	0	-0.364802	-1.027340	2.496168
40	6	0	-5.749730	-1.367728	0.219052
41	1	0	-6.019586	-2.190682	0.887655
42	1	0	-6.199224	-1.562852	-0.758747
43	1	0	-6.217430	-0.459648	0.617771
44	6	0	-1.709112	-0.198376	-2.504981
45	1	0	-0.642694	-0.429260	-2.582180
46	1	0	-1.830629	0.875435	-2.679411
47	1	0	-2.220986	-0.721941	-3.318637
48	6	0	-1.542976	4.202444	-0.637944
49	1	0	-2.129263	5.100386	-0.805979
50	6	0	-0.793210	2.450665	0.877292
51	6	0	-0.789484	1.859736	2.259834
52	1	0	0.179507	1.420194	2.509365
53	1	0	-1.544404	1.073269	2.349816
54	1	0	-1.017260	2.626941	3.004418
55	6	0	-0.044570	2.506778	-1.430251
56	1	0	0.557960	2.065390	-2.217375

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.57666907 a.u.

Excited State 1: Singlet-A 4.0117 eV 309.05 nm f=0.2336
<S**2>=0.000

```
     101 ->105         0.10551
     102 ->105        -0.15887
     103 ->104         0.65020
```

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72404190 a.u.

Results

Absorb Energy =	0.165 a.u.	4.490 eV	276.108 nm
Emission Energy =	0.147 a.u.	4.010 eV	309.171 nm
Stokes Shift =	0.018 a.u.	0.480 eV	33.062 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1161.66556976 a.u.
Lowest frequency = 19.0749

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.717248	0.680210	-0.059292
2	5	0	0.116420	-0.610840	-0.101401
3	6	0	1.075583	-1.819626	-0.166480
4	6	0	0.576804	-3.128405	-0.290533
5	1	0	-0.499006	-3.273671	-0.316132
6	6	0	1.418483	-4.219646	-0.385533
7	6	0	2.800048	-4.014133	-0.362030
8	1	0	3.476791	-4.859776	-0.441197
9	6	0	3.317841	-2.738213	-0.243022
10	1	0	4.394610	-2.621277	-0.238703
11	6	0	2.470391	-1.620152	-0.139489
12	6	0	2.992641	-0.251866	-0.006343
13	6	0	4.371132	-0.002965	0.100978
14	1	0	5.062041	-0.836619	0.094753
15	6	0	2.653429	2.151526	0.145111
16	1	0	1.987812	3.003657	0.167626
17	6	0	4.887718	1.271605	0.223369
18	1	0	5.959526	1.419223	0.304801
19	6	0	4.015966	2.357559	0.245107
20	6	0	2.117579	0.859372	0.019671
21	6	0	-2.067297	-1.191329	1.149476
22	6	0	-1.453867	-0.805721	-0.061357
23	6	0	-2.261502	-0.678200	-1.203941
24	6	0	-0.082017	1.879657	-0.172494
25	6	0	-1.389585	3.661868	0.749679
26	1	0	-1.828232	4.152983	1.613841
27	6	0	-0.996240	3.588905	-1.619143
28	1	0	-1.120139	4.006935	-2.613002

29	6	0	-3.641939	-0.861336	-1.110624
30	1	0	-4.248661	-0.759305	-2.008339
31	6	0	-4.259585	-1.177551	0.093665
32	6	0	-3.448923	-1.352517	1.213355
33	1	0	-3.904464	-1.637583	2.159558
34	1	0	1.015333	-5.222980	-0.481376
35	1	0	4.397131	3.369043	0.344174
36	6	0	-1.249595	-1.517321	2.379728
37	1	0	-0.942653	-2.569785	2.368861
38	1	0	-1.828189	-1.355953	3.294008
39	1	0	-0.335964	-0.923342	2.450799
40	6	0	-5.756029	-1.325953	0.188579
41	1	0	-6.036752	-2.090327	0.919211
42	1	0	-6.192050	-1.599656	-0.776335
43	1	0	-6.226723	-0.387553	0.504767
44	6	0	-1.678846	-0.370983	-2.563763
45	1	0	-0.596955	-0.525328	-2.594366
46	1	0	-1.872268	0.666022	-2.856590
47	1	0	-2.126583	-1.012715	-3.329266
48	6	0	-1.578089	4.202013	-0.515190
49	1	0	-2.166801	5.105935	-0.636197
50	6	0	-0.637686	2.501386	0.950964
51	6	0	-0.447262	1.968023	2.344439
52	1	0	0.525664	1.486254	2.466814
53	1	0	-1.215997	1.228501	2.588081
54	1	0	-0.524097	2.775442	3.077181
55	6	0	-0.246596	2.434730	-1.439957
56	1	0	0.228461	1.950241	-2.286260

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 4.4686 eV 277.46 nm f=0.2631
<S**2>=0.000
100 ->105 0.19096
103 ->104 0.62623
103 ->105 0.10661

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73709244 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57197337 a.u.

Excited State 1: Singlet-A 4.4930 eV 275.95 nm f=0.1672
<S**2>=0.000
100 ->104 -0.10939
100 ->105 0.21182
103 ->104 0.60971
103 ->105 0.11226

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.50891262 a.u.
Lowest frequency = 17.5842

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.728556	0.705394	-0.018734
2	5	0	0.124978	-0.648749	-0.105948
3	6	0	1.091442	-1.798695	-0.211243
4	6	0	0.655124	-3.124014	-0.359371
5	1	0	-0.414780	-3.312936	-0.389366
6	6	0	1.531762	-4.195016	-0.481194
7	6	0	2.924795	-3.956505	-0.461498
8	1	0	3.620529	-4.783011	-0.564714
9	6	0	3.403628	-2.674506	-0.312598
10	1	0	4.476975	-2.527924	-0.300593
11	6	0	2.524210	-1.553810	-0.175636
12	6	0	3.011468	-0.239973	0.014444
13	6	0	4.404596	0.069948	0.104474
14	1	0	5.128667	-0.727433	0.009523
15	6	0	2.595322	2.192012	0.363269
16	1	0	1.904759	3.016829	0.469640
17	6	0	4.861100	1.352037	0.319633
18	1	0	5.929060	1.534353	0.387637
19	6	0	3.959566	2.424127	0.461142
20	6	0	2.084179	0.900799	0.122500
21	6	0	-2.049826	-1.288461	1.138606
22	6	0	-1.442140	-0.837641	-0.053826
23	6	0	-2.258358	-0.648185	-1.183264
24	6	0	-0.087986	1.886475	-0.170544
25	6	0	-1.551081	3.589175	0.658474
26	1	0	-2.098838	4.034948	1.483986
27	6	0	-0.892200	3.618706	-1.652682
28	1	0	-0.920434	4.069250	-2.639533
29	6	0	-3.637455	-0.841537	-1.093554
30	1	0	-4.248843	-0.694399	-1.981770
31	6	0	-4.247709	-1.225942	0.094518
32	6	0	-3.430740	-1.457917	1.199365
33	1	0	-3.881255	-1.794337	2.130933
34	1	0	1.152017	-5.204732	-0.599623
35	1	0	4.325113	3.428340	0.645425
36	6	0	-1.227380	-1.661525	2.352021
37	1	0	-0.857698	-2.689819	2.267403
38	1	0	-1.825503	-1.602063	3.266147
39	1	0	-0.350581	-1.022644	2.479257
40	6	0	-5.742904	-1.385992	0.188463
41	1	0	-6.016675	-2.192050	0.875639
42	1	0	-6.182984	-1.605809	-0.788299
43	1	0	-6.215605	-0.469215	0.560308
44	6	0	-1.681222	-0.266228	-2.526154
45	1	0	-0.607144	-0.465466	-2.580067
46	1	0	-1.832551	0.796415	-2.740516
47	1	0	-2.163964	-0.832313	-3.329083
48	6	0	-1.615958	4.169872	-0.600690
49	1	0	-2.219566	5.058403	-0.756664
50	6	0	-0.786278	2.445795	0.905147
51	6	0	-0.725172	1.870707	2.293365

52	1	0	0.252084	1.431559	2.508307
53	1	0	-1.477429	1.087555	2.425679
54	1	0	-0.921192	2.646926	3.037408
55	6	0	-0.126049	2.483525	-1.430071
56	1	0	0.452662	2.042178	-2.234767

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58063368 a.u.

Excited State 1: Singlet-A 3.9939 eV 310.43 nm f=0.2423
<S**2>=0.000
101 ->105 0.10901
102 ->105 -0.14767
103 ->104 -0.65096

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72711989 a.u.

Results

Absorb Energy =	0.165 a.u.	4.493 eV	275.942 nm
Emission Energy =	0.146 a.u.	3.986 eV	311.042 nm
Stokes Shift =	0.019 a.u.	0.507 eV	35.100 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1161.66706206 a.u.
Lowest frequency = 15.0023

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.715231	0.680386	-0.062673
2	5	0	0.118702	-0.612543	-0.098938
3	6	0	1.081214	-1.819091	-0.154688
4	6	0	0.586289	-3.131015	-0.260991
5	1	0	-0.489048	-3.280258	-0.283160
6	6	0	1.431114	-4.221107	-0.341909
7	6	0	2.812222	-4.011249	-0.321055
8	1	0	3.491388	-4.855909	-0.388159
9	6	0	3.326429	-2.732206	-0.219268
10	1	0	4.402874	-2.612829	-0.214732
11	6	0	2.475630	-1.615121	-0.131380
12	6	0	2.994147	-0.243430	-0.018006
13	6	0	4.372947	0.011424	0.072714

14	1	0	5.067291	-0.819309	0.066468
15	6	0	2.647703	2.160427	0.111431
16	1	0	1.979454	3.010560	0.130946
17	6	0	4.885988	1.289186	0.177030
18	1	0	5.957993	1.441438	0.245829
19	6	0	4.010492	2.372360	0.196417
20	6	0	2.115367	0.865120	0.004308
21	6	0	-2.072318	-1.177668	1.150171
22	6	0	-1.451533	-0.810382	-0.062584
23	6	0	-2.252145	-0.701181	-1.212273
24	6	0	-0.091027	1.876027	-0.167949
25	6	0	-1.387709	3.658121	0.770239
26	1	0	-1.808293	4.154325	1.640443
27	6	0	-1.049979	3.567263	-1.606905
28	1	0	-1.199901	3.976007	-2.600990
29	6	0	-3.633398	-0.882926	-1.124661
30	1	0	-4.234549	-0.795098	-2.027598
31	6	0	-4.258480	-1.180389	0.080874
32	6	0	-3.454466	-1.338057	1.208184
33	1	0	-3.915714	-1.608553	2.155874
34	1	0	1.030936	-5.226819	-0.423864
35	1	0	4.388970	3.386106	0.281183
36	6	0	-1.262225	-1.485934	2.389858
37	1	0	-0.973301	-2.543519	2.405316
38	1	0	-1.839333	-1.293108	3.298932
39	1	0	-0.339190	-0.905377	2.447750
40	6	0	-5.755494	-1.327714	0.169155
41	1	0	-6.040003	-2.086179	0.904422
42	1	0	-6.186520	-1.608393	-0.795939
43	1	0	-6.227495	-0.386902	0.476052
44	6	0	-1.661501	-0.416134	-2.573681
45	1	0	-0.576908	-0.551878	-2.591037
46	1	0	-1.870321	0.609741	-2.894026
47	1	0	-2.090993	-1.083449	-3.327708
48	6	0	-1.609895	4.185996	-0.494531
49	1	0	-2.207155	5.085092	-0.609162
50	6	0	-0.623643	2.503977	0.963403
51	6	0	-0.396595	1.985477	2.357315
52	1	0	0.573538	1.493216	2.456584
53	1	0	-1.166147	1.258998	2.635447
54	1	0	-0.441532	2.803165	3.081204
55	6	0	-0.288452	2.419474	-1.435796
56	1	0	0.169744	1.931462	-2.289206

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 4.4740 eV 277.12 nm f=0.2499
<S**2>=0.000
100 ->105 0.19273
103 ->104 0.62490
103 ->105 0.10946

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1161.73872046 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1161.57346430 a.u.

Excited State 1: Singlet-A 4.4954 eV 275.80 nm f=0.1672
<S**2>=0.000
100 ->104 -0.10728
100 ->105 0.20836
103 ->104 0.61017
103 ->105 0.11461

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1161.51129020 a.u.
Lowest frequency = 17.2931

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.725103	0.705766	-0.021302
2	5	0	0.127697	-0.649467	-0.103544
3	6	0	1.098513	-1.797645	-0.202047
4	6	0	0.667447	-3.124362	-0.340727
5	1	0	-0.401712	-3.318186	-0.367924
6	6	0	1.548147	-4.193985	-0.455990
7	6	0	2.940586	-3.949862	-0.438343
8	1	0	3.639113	-4.774800	-0.535220
9	6	0	3.415281	-2.666061	-0.299335
10	1	0	4.488086	-2.516058	-0.288291
11	6	0	2.530784	-1.545637	-0.170052
12	6	0	3.013086	-0.230708	0.006827
13	6	0	4.407557	0.086123	0.085907
14	1	0	5.134558	-0.708276	-0.010860
15	6	0	2.588025	2.201599	0.343915
16	1	0	1.895293	3.024869	0.447942
17	6	0	4.858304	1.370507	0.292622
18	1	0	5.925682	1.558794	0.353309
19	6	0	3.952286	2.439675	0.434240
20	6	0	2.081174	0.908171	0.113007
21	6	0	-2.050602	-1.284180	1.139067
22	6	0	-1.439071	-0.843071	-0.054967
23	6	0	-2.251065	-0.664540	-1.189414
24	6	0	-0.098462	1.883062	-0.168163
25	6	0	-1.556984	3.583938	0.673275
26	1	0	-2.094268	4.032135	1.504320
27	6	0	-0.931994	3.603673	-1.647732
28	1	0	-0.976570	4.048663	-2.636455
29	6	0	-3.630566	-0.858108	-1.103174
30	1	0	-4.238713	-0.719537	-1.994973
31	6	0	-4.245027	-1.232331	0.086322
32	6	0	-3.431810	-1.454074	1.196259
33	1	0	-3.885477	-1.782466	2.129116
34	1	0	1.171929	-5.205866	-0.566732
35	1	0	4.314631	3.446345	0.611463

36	6	0	-1.232571	-1.647836	2.358323
37	1	0	-0.877622	-2.682640	2.290196
38	1	0	-1.829214	-1.565733	3.271574
39	1	0	-0.347296	-1.018798	2.474814
40	6	0	-5.740482	-1.392604	0.176343
41	1	0	-6.015938	-2.193366	0.868942
42	1	0	-6.177072	-1.619711	-0.800272
43	1	0	-6.214795	-0.473354	0.539863
44	6	0	-1.669528	-0.294640	-2.533981
45	1	0	-0.591852	-0.475843	-2.577176
46	1	0	-1.837237	0.761466	-2.767613
47	1	0	-2.136617	-0.881613	-3.331164
48	6	0	-1.642732	4.157536	-0.588129
49	1	0	-2.252230	5.042717	-0.740010
50	6	0	-0.783366	2.445173	0.914809
51	6	0	-0.700127	1.877871	2.305240
52	1	0	0.280167	1.439565	2.507380
53	1	0	-1.450316	1.095787	2.454876
54	1	0	-0.884429	2.658391	3.047655
55	6	0	-0.157440	2.472991	-1.430234
56	1	0	0.411511	2.030416	-2.241122

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1) SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1161.58228793 a.u.

Excited State 1: Singlet-A 3.9867 eV 310.99 nm f=0.2462 <S**2>=0.000
101 ->105 0.10614
102 ->105 -0.14668
103 ->104 -0.65106

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1161.72840736 a.u.

Results

Absorb Energy =	0.165 a.u.	4.497 eV	275.713 nm
Emission Energy =	0.146 a.u.	3.976 eV	311.823 nm
Stokes Shift =	0.019 a.u.	0.521 eV	36.109 nm

5.1.6 Compound 4 – GS1-0-R

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1261.59805459 a.u.
Lowest frequency = 26.9104

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.121438	-0.647803	0.221799
2	5	0	-0.629067	0.794494	0.569893
3	6	0	-2.052953	0.971519	-0.188042
4	6	0	-2.514161	2.189211	-0.696655
5	1	0	-1.869782	3.061986	-0.621085
6	6	0	-3.760361	2.319728	-1.297845
7	6	0	-4.576685	1.199645	-1.425761
8	1	0	-5.545159	1.275216	-1.914219
9	6	0	-4.139528	-0.025427	-0.944207
10	1	0	-4.767140	-0.899722	-1.089461
11	6	0	-2.895471	-0.150203	-0.307953
12	6	0	-2.423783	-1.454891	0.199926
13	6	0	-3.313215	-2.500882	0.458075
14	1	0	-4.378432	-2.311188	0.366424
15	6	0	-0.617844	-2.978992	0.748674
16	1	0	0.441249	-3.166568	0.884302
17	6	0	-2.891304	-3.767380	0.836683
18	1	0	-3.615181	-4.553467	1.030493
19	6	0	-1.526028	-4.002076	0.964262
20	6	0	-1.031095	-1.680848	0.386687
21	6	0	1.008931	1.916244	-1.133442
22	6	0	0.437511	1.958231	0.145716
23	6	0	0.768204	3.075208	0.946649
24	6	0	2.227841	-0.828834	0.971640
25	6	0	1.912651	-0.269774	2.332957
26	1	0	2.580591	-0.698386	3.087697
27	1	0	2.049698	0.817106	2.344265
28	1	0	0.874762	-0.448729	2.611908
29	6	0	1.592699	-1.564058	-1.252614
30	6	0	1.234778	-1.007722	-0.005068
31	6	0	0.556291	-1.787565	-2.321676
32	1	0	1.030474	-1.967549	-3.291086
33	1	0	-0.078935	-2.650003	-2.091381
34	1	0	-0.113538	-0.927757	-2.409131
35	6	0	3.546023	-1.184361	0.677920
36	1	0	4.304730	-1.041514	1.445754
37	6	0	3.917281	-1.718690	-0.548256
38	6	0	2.916525	-1.910035	-1.498622
39	1	0	3.176537	-2.330910	-2.468415
40	6	0	1.651539	4.045984	0.461829
41	1	0	1.896551	4.894754	1.097933
42	6	0	2.215088	3.961716	-0.804700
43	1	0	2.899145	4.731659	-1.153284
44	6	0	1.883338	2.884003	-1.614275
45	1	0	2.301142	2.795119	-2.614359
46	6	0	5.353738	-2.060219	-0.852546
47	1	0	5.432314	-2.978283	-1.444273
48	1	0	5.842580	-1.263883	-1.427332
49	1	0	5.933006	-2.200572	0.065177
50	1	0	-4.089352	3.284312	-1.677303
51	1	0	-1.161723	-4.983881	1.257012
52	9	0	-0.894355	0.829807	1.989204
53	6	0	0.192223	3.292362	2.330126
54	1	0	-0.900446	3.306480	2.313946
55	1	0	0.468112	2.489642	3.016312

56	1	0	0.544407	4.244249	2.742789
57	1	0	0.755566	1.084418	-1.784463

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 3.8766 eV 319.83 nm f=0.2605 <S**2>=0.000

108 ->109	0.67381
108 ->113	0.10302

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.68816334 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.54618311 a.u.

Excited State 1: Singlet-A 3.8739 eV 320.05 nm f=0.1907 <S**2>=0.000

108 ->109	0.67664

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.45963620 a.u.
Lowest frequency = 35.2275

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.167753	-0.636904	0.340824
2	5	0	-0.611751	0.893540	0.583214
3	6	0	-2.010307	1.092182	-0.191666
4	6	0	-2.428970	2.328034	-0.649214
5	1	0	-1.742675	3.169155	-0.578296
6	6	0	-3.700303	2.536855	-1.211025
7	6	0	-4.574420	1.453557	-1.300098
8	1	0	-5.563875	1.588015	-1.734139
9	6	0	-4.198386	0.200927	-0.852840
10	1	0	-4.900511	-0.619844	-0.955468
11	6	0	-2.903982	-0.022761	-0.287912
12	6	0	-2.506425	-1.308198	0.194549
13	6	0	-3.400142	-2.420112	0.278264
14	1	0	-4.442676	-2.275871	0.023737
15	6	0	-0.730108	-2.895356	0.941895
16	1	0	0.306131	-3.052001	1.218968
17	6	0	-2.990439	-3.673583	0.692713
18	1	0	-3.725450	-4.473515	0.751885
19	6	0	-1.653523	-3.936727	1.044074
20	6	0	-1.111624	-1.610641	0.522295

21	6	0	1.007864	1.846260	-1.207858
22	6	0	0.538802	1.938396	0.109473
23	6	0	1.045764	2.997759	0.892711
24	6	0	2.205912	-0.850876	0.963498
25	6	0	1.992942	-0.233716	2.320976
26	1	0	2.482572	-0.835313	3.095295
27	1	0	2.432677	0.769283	2.359744
28	1	0	0.936828	-0.129357	2.565224
29	6	0	1.410756	-1.698614	-1.184157
30	6	0	1.155427	-1.066244	0.056331
31	6	0	0.308627	-1.958773	-2.177354
32	1	0	0.724284	-2.129502	-3.174289
33	1	0	-0.275947	-2.841234	-1.895932
34	1	0	-0.395582	-1.123867	-2.230171
35	6	0	3.492331	-1.261864	0.607419
36	1	0	4.298929	-1.103555	1.321078
37	6	0	3.773427	-1.862651	-0.609709
38	6	0	2.709933	-2.068307	-1.494136
39	1	0	2.903122	-2.531629	-2.459665
40	6	0	2.001916	3.865208	0.353001
41	1	0	2.382939	4.674665	0.972830
42	6	0	2.468886	3.727490	-0.947442
43	1	0	3.212983	4.417358	-1.337801
44	6	0	1.957989	2.708866	-1.740763
45	1	0	2.292693	2.587676	-2.767977
46	6	0	5.170829	-2.290654	-0.974181
47	1	0	5.235734	-3.375872	-1.118247
48	1	0	5.501882	-1.824077	-1.909141
49	1	0	5.886276	-2.015835	-0.193855
50	1	0	-3.990389	3.517720	-1.577950
51	1	0	-1.349428	-4.915922	1.397190
52	9	0	-0.854700	0.961018	1.996579
53	6	0	0.586633	3.263994	2.310694
54	1	0	-0.500826	3.335377	2.374400
55	1	0	0.876141	2.460859	2.992626
56	1	0	1.019580	4.200121	2.679508
57	1	0	0.603460	1.065937	-1.847835

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1) SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.55443790 a.u.

Excited State 1: Singlet-A 3.3731 eV 367.57 nm f=0.2333 <S**2>=0.000
108 ->109 0.68878

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.67813335 a.u.

Results

Absorb Energy =	0.142 a.u.	3.863 eV	320.913 nm
Emission Energy =	0.124 a.u.	3.366 eV	368.351 nm

Stokes Shift = | 0.018 a.u. | 0.498 eV | 47.438 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1261.62594324 a.u.
Lowest frequency = 28.5559

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.115042	-0.648184	0.226373
2	5	0	-0.633095	0.787059	0.572184
3	6	0	-2.062620	0.954585	-0.177206
4	6	0	-2.538356	2.173643	-0.670641
5	1	0	-1.902365	3.051948	-0.587523
6	6	0	-3.789135	2.299741	-1.264104
7	6	0	-4.595891	1.172951	-1.399149
8	1	0	-5.567358	1.244986	-1.881192
9	6	0	-4.145401	-0.053293	-0.931998
10	1	0	-4.767897	-0.930146	-1.082176
11	6	0	-2.896174	-0.173752	-0.303432
12	6	0	-2.410620	-1.478861	0.191131
13	6	0	-3.290504	-2.537396	0.437599
14	1	0	-4.357463	-2.360378	0.342356
15	6	0	-0.590451	-2.987774	0.734616
16	1	0	0.470051	-3.166269	0.871382
17	6	0	-2.856139	-3.801825	0.808584
18	1	0	-3.571444	-4.597436	0.993055
19	6	0	-1.488010	-4.022494	0.939735
20	6	0	-1.015773	-1.690914	0.379629
21	6	0	0.980459	1.919112	-1.140658
22	6	0	0.419501	1.960648	0.143730
23	6	0	0.746018	3.084543	0.936948
24	6	0	2.235524	-0.816259	0.980512
25	6	0	1.914716	-0.268403	2.345201
26	1	0	2.596138	-0.682588	3.095188
27	1	0	2.024301	0.821486	2.360828
28	1	0	0.883070	-0.473422	2.628926
29	6	0	1.611570	-1.542130	-1.249671
30	6	0	1.246558	-0.995825	0.000069
31	6	0	0.579643	-1.774899	-2.321316
32	1	0	1.057609	-1.963742	-3.286667
33	1	0	-0.054869	-2.636085	-2.084596
34	1	0	-0.090031	-0.916336	-2.421527
35	6	0	3.557527	-1.161286	0.688629
36	1	0	4.312379	-1.021579	1.460301
37	6	0	3.936575	-1.685116	-0.540454
38	6	0	2.939159	-1.875317	-1.495493
39	1	0	3.204091	-2.289850	-2.466323
40	6	0	1.614368	4.063161	0.438858
41	1	0	1.856437	4.917414	1.068098
42	6	0	2.167726	3.979203	-0.832612
43	1	0	2.838759	4.755455	-1.191049
44	6	0	1.839974	2.894012	-1.634867

45	1	0	2.248666	2.806067	-2.638531
46	6	0	5.375313	-2.019929	-0.841021
47	1	0	5.458671	-2.933736	-1.437818
48	1	0	5.861965	-1.218662	-1.410157
49	1	0	5.951575	-2.162217	0.077851
50	1	0	-4.130370	3.264974	-1.629937
51	1	0	-1.114619	-5.002135	1.227043
52	9	0	-0.897490	0.823925	1.997306
53	6	0	0.183320	3.303637	2.325817
54	1	0	-0.909666	3.309156	2.322515
55	1	0	0.477170	2.508927	3.014038
56	1	0	0.530286	4.260561	2.729557
57	1	0	0.729843	1.081685	-1.785521

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 3.8832 eV 319.28 nm f=0.2612
<S**2>=0.000
108 ->109 0.67964

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.71618757 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.57410375 a.u.

Excited State 1: Singlet-A 3.8774 eV 319.76 nm f=0.1878
<S**2>=0.000
108 ->109 0.67977

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.48966447 a.u.
Lowest frequency = 27.9295

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.172535	-0.646735	0.333458
2	5	0	-0.609201	0.880965	0.578815
3	6	0	-2.009176	1.094927	-0.188627
4	6	0	-2.427231	2.336617	-0.628613
5	1	0	-1.735463	3.173589	-0.554889
6	6	0	-3.706261	2.559561	-1.172206
7	6	0	-4.588465	1.481124	-1.260150
8	1	0	-5.582177	1.625731	-1.680132
9	6	0	-4.215425	0.222023	-0.828826
10	1	0	-4.923793	-0.593103	-0.931011

11	6	0	-2.912035	-0.015934	-0.281620
12	6	0	-2.517400	-1.303408	0.185758
13	6	0	-3.424018	-2.408306	0.277510
14	1	0	-4.472018	-2.247522	0.057852
15	6	0	-0.741296	-2.920167	0.873214
16	1	0	0.296797	-3.094647	1.131264
17	6	0	-3.017149	-3.672236	0.656619
18	1	0	-3.757407	-4.466264	0.721150
19	6	0	-1.671796	-3.954051	0.966696
20	6	0	-1.116371	-1.619029	0.490766
21	6	0	1.002035	1.834670	-1.212203
22	6	0	0.543135	1.924038	0.109587
23	6	0	1.060791	2.977998	0.893202
24	6	0	2.194823	-0.875000	0.988081
25	6	0	1.964451	-0.298204	2.360916
26	1	0	2.409361	-0.944503	3.125634
27	1	0	2.441837	0.683998	2.450400
28	1	0	0.906668	-0.163484	2.580285
29	6	0	1.432912	-1.668649	-1.190919
30	6	0	1.159201	-1.069263	0.061157
31	6	0	0.345652	-1.909995	-2.205367
32	1	0	0.774283	-2.043714	-3.201964
33	1	0	-0.229375	-2.809424	-1.960335
34	1	0	-0.368101	-1.082403	-2.240066
35	6	0	3.488764	-1.270519	0.638764
36	1	0	4.284958	-1.128343	1.366857
37	6	0	3.788880	-1.838779	-0.590032
38	6	0	2.737586	-2.027871	-1.492662
39	1	0	2.945166	-2.467865	-2.465754
40	6	0	2.014932	3.845369	0.347886
41	1	0	2.404586	4.650838	0.966938
42	6	0	2.469699	3.711944	-0.957729
43	1	0	3.212021	4.400969	-1.351833
44	6	0	1.949855	2.696743	-1.750842
45	1	0	2.275749	2.579011	-2.781105
46	6	0	5.194362	-2.243173	-0.950130
47	1	0	5.251235	-3.305536	-1.212422
48	1	0	5.562014	-1.680793	-1.815991
49	1	0	5.883940	-2.065314	-0.120522
50	1	0	-3.996524	3.545751	-1.523921
51	1	0	-1.368759	-4.944297	1.288442
52	9	0	-0.862675	0.948767	1.995401
53	6	0	0.617710	3.239857	2.317104
54	1	0	-0.467920	3.332639	2.391313
55	1	0	0.899854	2.425943	2.989005
56	1	0	1.069856	4.164144	2.691037
57	1	0	0.592052	1.056290	-1.851143

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.58450615 a.u.

Excited State 1: Singlet-A 3.3376 eV 371.48 nm f=0.2345
<S**2>=0.000
108 ->109 0.68987

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.70535981 a.u.

Results

Absorb Energy =	0.142 a.u.	3.866 eV	320.679 nm
Emission Energy =	0.121 a.u.	3.289 eV	377.013 nm
Stokes Shift =	0.021 a.u.	0.578 eV	56.333 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1261.63511467 a.u.
Lowest frequency = 25.3313

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.112270	-0.650427	0.227035
2	5	0	-0.634452	0.781777	0.573915
3	6	0	-2.068843	0.945475	-0.166880
4	6	0	-2.553889	2.166943	-0.646325
5	1	0	-1.922829	3.048183	-0.556480
6	6	0	-3.808042	2.292376	-1.233062
7	6	0	-4.609614	1.162433	-1.374970
8	1	0	-5.583433	1.233939	-1.851885
9	6	0	-4.151130	-0.065727	-0.920474
10	1	0	-4.771245	-0.943429	-1.074783
11	6	0	-2.897860	-0.185858	-0.298902
12	6	0	-2.404744	-1.492937	0.183545
13	6	0	-3.279446	-2.558573	0.420898
14	1	0	-4.347270	-2.387568	0.325666
15	6	0	-0.576603	-2.996731	0.714630
16	1	0	0.484741	-3.171513	0.849453
17	6	0	-2.838330	-3.823522	0.781770
18	1	0	-3.549135	-4.624568	0.959051
19	6	0	-1.468735	-4.037910	0.911368
20	6	0	-1.008446	-1.698777	0.370204
21	6	0	0.965063	1.918065	-1.148376
22	6	0	0.410266	1.960073	0.139060
23	6	0	0.733818	3.088900	0.926651
24	6	0	2.236013	-0.812347	0.990818
25	6	0	1.907370	-0.277501	2.358998
26	1	0	2.603159	-0.676196	3.103797
27	1	0	1.986492	0.814812	2.379705
28	1	0	0.883375	-0.511662	2.647792
29	6	0	1.626485	-1.527764	-1.246941
30	6	0	1.252734	-0.990884	0.004755
31	6	0	0.601384	-1.763845	-2.324624
32	1	0	1.085125	-1.940850	-3.289106
33	1	0	-0.023570	-2.634372	-2.096628
34	1	0	-0.077355	-0.912148	-2.422312

35	6	0	3.562152	-1.146880	0.702409
36	1	0	4.312537	-1.008486	1.478429
37	6	0	3.949935	-1.659835	-0.528532
38	6	0	2.957425	-1.849327	-1.489659
39	1	0	3.229244	-2.255900	-2.461823
40	6	0	1.594318	4.071033	0.420902
41	1	0	1.834347	4.928945	1.045645
42	6	0	2.142496	3.985834	-0.852892
43	1	0	2.807103	4.764715	-1.217037
44	6	0	1.816685	2.896207	-1.650401
45	1	0	2.220210	2.808025	-2.656055
46	6	0	5.390693	-1.989672	-0.824665
47	1	0	5.483824	-2.945704	-1.349729
48	1	0	5.852119	-1.227296	-1.463518
49	1	0	5.982075	-2.048779	0.093377
50	1	0	-4.156248	3.259027	-1.588010
51	1	0	-1.090186	-5.017843	1.190257
52	9	0	-0.892277	0.820906	2.002544
53	6	0	0.176592	3.311197	2.317243
54	1	0	-0.916260	3.300594	2.320785
55	1	0	0.487969	2.527745	3.010970
56	1	0	0.511535	4.276271	2.710869
57	1	0	0.715817	1.077331	-1.789455

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 3.8919 eV 318.57 nm f=0.2526
<S**2>=0.000
108 ->109 0.68003

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.72564001 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.58305633 a.u.

Excited State 1: Singlet-A 3.8863 eV 319.03 nm f=0.1884
<S**2>=0.000
108 ->109 0.67980

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.49973160 a.u.
Lowest frequency = 22.4449

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	7	0	-0.179691	-0.649011	0.328824
2	5	0	-0.605806	0.879620	0.577018
3	6	0	-2.006089	1.106767	-0.185308
4	6	0	-2.419730	2.352916	-0.616564
5	1	0	-1.723081	3.185896	-0.541823
6	6	0	-3.701378	2.587364	-1.150703
7	6	0	-4.591309	1.514554	-1.238463
8	1	0	-5.586607	1.667858	-1.651080
9	6	0	-4.224105	0.251001	-0.815373
10	1	0	-4.938797	-0.558479	-0.917091
11	6	0	-2.917427	0.001052	-0.277591
12	6	0	-2.529389	-1.289960	0.181308
13	6	0	-3.444755	-2.389278	0.273001
14	1	0	-4.493536	-2.219162	0.064591
15	6	0	-0.759552	-2.925812	0.842482
16	1	0	0.278679	-3.111308	1.091807
17	6	0	-3.043701	-3.659191	0.636491
18	1	0	-3.788545	-4.448734	0.700062
19	6	0	-1.696968	-3.953064	0.932373
20	6	0	-1.127292	-1.616726	0.476424
21	6	0	0.999574	1.834422	-1.214954
22	6	0	0.553802	1.915869	0.112252
23	6	0	1.092655	2.954595	0.902049
24	6	0	2.182846	-0.902106	0.997199
25	6	0	1.944557	-0.365397	2.385357
26	1	0	2.273614	-1.092860	3.136216
27	1	0	2.525893	0.548524	2.550424
28	1	0	0.897647	-0.126169	2.562237
29	6	0	1.432981	-1.650774	-1.201598
30	6	0	1.153579	-1.074334	0.059685
31	6	0	0.351135	-1.874808	-2.225990
32	1	0	0.784805	-1.991536	-3.222342
33	1	0	-0.223500	-2.779582	-1.999957
34	1	0	-0.363207	-1.047434	-2.250782
35	6	0	3.479135	-1.291080	0.647319
36	1	0	4.271255	-1.163754	1.382410
37	6	0	3.785544	-1.835799	-0.590748
38	6	0	2.738944	-2.006693	-1.502718
39	1	0	2.951621	-2.428836	-2.482418
40	6	0	2.051003	3.817110	0.355383
41	1	0	2.457058	4.610956	0.978597
42	6	0	2.490619	3.692722	-0.956411
43	1	0	3.236454	4.377472	-1.350860
44	6	0	1.951980	2.690970	-1.754661
45	1	0	2.266650	2.580093	-2.789088
46	6	0	5.192459	-2.234908	-0.951019
47	1	0	5.249137	-3.293216	-1.228555
48	1	0	5.562682	-1.660702	-1.807771
49	1	0	5.878739	-2.069407	-0.116335
50	1	0	-3.987709	3.577160	-1.495117
51	1	0	-1.398695	-4.948915	1.240856
52	9	0	-0.862877	0.947178	1.995865
53	6	0	0.671523	3.205924	2.334519
54	1	0	-0.411600	3.313350	2.424989
55	1	0	0.953543	2.381306	2.993378
56	1	0	1.140777	4.119573	2.712726
57	1	0	0.575632	1.066237	-1.857163

Step6

```
 Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
 After PCM corrections, the energy is -1261.59465674 a.u.

 Excited State   1:      Singlet-A      3.3219 eV  373.24 nm  f=0.2348
<S**2>=0.000
     108 ->109         0.69005

Step7

  Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

 SCF Done: E(RCAM-B3LYP) = -1261.71423776 a.u.

                             Results
 ------------------------------------------------------------------
     Absorb Energy     =  | 0.143 a.u. | 3.880 eV | 319.555 nm
 --------------------------|------------|----------|----------------
     Emission Energy   =  | 0.120 a.u. | 3.254 eV | 381.025 nm
 --------------------------|------------|----------|----------------
     Stokes Shift      =  | 0.023 a.u. | 0.626 eV | 61.470 nm
 ------------------------------------------------------------------
```

5.1.7 Compound 4 – GS1-180-R

THF

Step1

```
 Method: cam-b3lyp/6-31G(d)
 Solvent : TetraHydroFuran
 SCF Done: E(RCAM-B3LYP) = -1261.62675907 a.u.
 Lowest frequency =  32.3599

                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          7           0       -0.161004   -0.614427    0.294409
      2          5           0       -0.593700    0.824779    0.713048
      3          6           0       -2.021483    1.116620    0.006121
      4          6           0       -2.444370    2.390302   -0.386969
      5          1           0       -1.763317    3.227376   -0.252017
      6          6           0       -3.696396    2.620037   -0.945512
      7          6           0       -4.561893    1.547103   -1.141894
      8          1           0       -5.536304    1.701199   -1.597965
      9          6           0       -4.168651    0.270896   -0.766207
     10          1           0       -4.840243   -0.560163   -0.958886
     11          6           0       -2.916436    0.043801   -0.173800
     12          6           0       -2.499903   -1.312575    0.240356
     13          6           0       -3.435656   -2.332853    0.437782
     14          1           0       -4.491638   -2.093850    0.358600
     15          6           0       -0.763936   -2.943923    0.699612
     16          1           0        0.285939   -3.185466    0.822712
     17          6           0       -3.069986   -3.636235    0.742015
     18          1           0       -3.827455   -4.399936    0.889407
     19          6           0       -1.715879   -3.937495    0.857452
     20          6           0       -1.118832   -1.611201    0.407857
```

21	6	0	1.035499	2.398833	-0.802706
22	6	0	0.531699	1.984476	0.450139
23	6	0	0.981419	2.700529	1.569281
24	1	0	0.587355	2.415024	2.538572
25	6	0	2.202163	-0.916322	0.976152
26	6	0	1.956804	-0.471516	2.396100
27	1	0	2.344263	-1.221694	3.095424
28	1	0	2.478002	0.468099	2.607593
29	1	0	0.899907	-0.305255	2.594480
30	6	0	1.477467	-1.570920	-1.246202
31	6	0	1.175332	-1.022376	0.022849
32	6	0	0.400728	-1.800681	-2.274944
33	1	0	0.832548	-1.881809	-3.276762
34	1	0	-0.146826	-2.727654	-2.069783
35	1	0	-0.333512	-0.993498	-2.270220
36	6	0	3.503218	-1.288013	0.624707
37	1	0	4.287079	-1.194222	1.374548
38	6	0	3.824366	-1.787705	-0.629312
39	6	0	2.785021	-1.936172	-1.546837
40	1	0	2.999772	-2.346656	-2.531768
41	6	0	1.894296	3.747825	1.491078
42	1	0	2.210141	4.266336	2.393261
43	6	0	2.388882	4.129283	0.250858
44	1	0	3.098808	4.947460	0.160803
45	6	0	1.948674	3.455019	-0.881446
46	1	0	2.318425	3.756565	-1.859707
47	6	0	5.241702	-2.148884	-0.993355
48	1	0	5.278512	-3.042194	-1.624862
49	1	0	5.729812	-1.340393	-1.550935
50	1	0	5.845957	-2.339443	-0.101572
51	1	0	-3.994379	3.624631	-1.235082
52	1	0	-1.396144	-4.948824	1.095319
53	6	0	0.631438	1.732363	-2.095492
54	1	0	-0.413150	1.417172	-2.077815
55	1	0	1.237702	0.840490	-2.282004
56	1	0	0.772800	2.409172	-2.944898
57	9	0	-0.862248	0.795925	2.150149

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 3.8663 eV 320.68 nm f=0.2588
<S**2>=0.000
108 ->109 0.68077

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.71669389 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.57508140 a.u.

Excited State 1: Singlet-A 3.8586 eV 321.32 nm f=0.1861
<S**2>=0.000

108 ->109 -0.68060

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.49133178 a.u.
Lowest frequency = 31.8228

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.173977	-0.628503	0.387681
2	5	0	-0.590845	0.883849	0.714559
3	6	0	-2.001440	1.161453	-0.009677
4	6	0	-2.422374	2.436988	-0.337691
5	1	0	-1.723685	3.261410	-0.208810
6	6	0	-3.710081	2.708709	-0.834519
7	6	0	-4.600041	1.644022	-0.990740
8	1	0	-5.601750	1.826014	-1.375662
9	6	0	-4.226162	0.353516	-0.668336
10	1	0	-4.944550	-0.445828	-0.814840
11	6	0	-2.914305	0.065501	-0.166673
12	6	0	-2.526073	-1.254009	0.208163
13	6	0	-3.437946	-2.358139	0.226276
14	1	0	-4.481446	-2.182220	-0.002667
15	6	0	-0.767591	-2.916622	0.827127
16	1	0	0.267670	-3.110488	1.083522
17	6	0	-3.043606	-3.641943	0.544821
18	1	0	-3.788879	-4.433777	0.556354
19	6	0	-1.704357	-3.947384	0.861619
20	6	0	-1.129389	-1.597302	0.501689
21	6	0	1.070467	2.317648	-0.873372
22	6	0	0.572904	1.977434	0.402660
23	6	0	1.056188	2.724096	1.486654
24	1	0	0.665393	2.494816	2.472456
25	6	0	2.197355	-0.882177	1.015000
26	6	0	1.975910	-0.405395	2.428246
27	1	0	2.322387	-1.166273	3.137539
28	1	0	2.548925	0.506371	2.625690
29	1	0	0.929879	-0.185866	2.632785
30	6	0	1.413091	-1.639981	-1.170975
31	6	0	1.151204	-1.050608	0.090770
32	6	0	0.318393	-1.922139	-2.167481
33	1	0	0.730096	-1.983074	-3.178601
34	1	0	-0.174050	-2.874794	-1.945073
35	1	0	-0.456536	-1.153307	-2.153866
36	6	0	3.490729	-1.250353	0.637623
37	1	0	4.293389	-1.122870	1.361359
38	6	0	3.782483	-1.782068	-0.609887
39	6	0	2.719391	-1.975136	-1.496773
40	1	0	2.916431	-2.404828	-2.476643
41	6	0	1.999615	3.737338	1.350976
42	1	0	2.342211	4.286455	2.224548
43	6	0	2.490652	4.045933	0.088745
44	1	0	3.224836	4.836145	-0.044765
45	6	0	2.016657	3.338065	-1.008649
46	1	0	2.383751	3.584884	-2.003049
47	6	0	5.189945	-2.145470	-1.003537

48	1	0	5.246950	-3.168875	-1.389896
49	1	0	5.566102	-1.484654	-1.793305
50	1	0	5.873348	-2.067316	-0.153641
51	1	0	-4.002043	3.721509	-1.097969
52	1	0	-1.411647	-4.953472	1.140743
53	6	0	0.623736	1.606153	-2.127922
54	1	0	-0.401671	1.243310	-2.038259
55	1	0	1.264902	0.744359	-2.342660
56	1	0	0.674899	2.273698	-2.994689
57	9	0	-0.844998	0.872241	2.140889

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.58583733 a.u.

Excited State 1: Singlet-A 3.3133 eV 374.20 nm f=0.2327
<S**2>=0.000
108 ->109 0.69007

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.70586674 a.u.

Results

Absorb Energy =	0.142 a.u.	3.853 eV	321.747 nm
Emission Energy =	0.120 a.u.	3.266 eV	379.602 nm
Stokes Shift =	0.022 a.u.	0.587 eV	57.855 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1261.63602858 a.u.
Lowest frequency = 32.3830

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.160238	-0.617149	0.291817
2	5	0	-0.593186	0.820432	0.707700
3	6	0	-2.022386	1.113321	0.004107
4	6	0	-2.448124	2.387356	-0.386229
5	1	0	-1.766725	3.225043	-0.256440
6	6	0	-3.703877	2.617626	-0.936496
7	6	0	-4.570687	1.544595	-1.127533
8	1	0	-5.548088	1.698892	-1.576613
9	6	0	-4.174808	0.267951	-0.755525
10	1	0	-4.848553	-0.562077	-0.944322

11	6	0	-2.918409	0.040139	-0.171549
12	6	0	-2.499271	-1.317281	0.237871
13	6	0	-3.434117	-2.339458	0.433905
14	1	0	-4.490610	-2.102307	0.357115
15	6	0	-0.760532	-2.949251	0.686309
16	1	0	0.289719	-3.191161	0.804724
17	6	0	-3.066363	-3.643503	0.732669
18	1	0	-3.822540	-4.408514	0.878604
19	6	0	-1.711425	-3.944198	0.843049
20	6	0	-1.117218	-1.615289	0.401258
21	6	0	1.029714	2.405735	-0.801658
22	6	0	0.530844	1.982395	0.450601
23	6	0	0.983679	2.692470	1.572658
24	1	0	0.595941	2.400169	2.542471
25	6	0	2.201257	-0.923731	0.980039
26	6	0	1.951718	-0.491153	2.403249
27	1	0	2.310817	-1.260405	3.096919
28	1	0	2.497242	0.430045	2.633876
29	1	0	0.897724	-0.298876	2.592249
30	6	0	1.485786	-1.559095	-1.251139
31	6	0	1.178362	-1.022802	0.022158
32	6	0	0.413173	-1.783536	-2.285452
33	1	0	0.848387	-1.855057	-3.286310
34	1	0	-0.130862	-2.714744	-2.090232
35	1	0	-0.324005	-0.979125	-2.276689
36	6	0	3.504895	-1.289888	0.630005
37	1	0	4.285810	-1.201760	1.383407
38	6	0	3.831253	-1.777480	-0.627363
39	6	0	2.795131	-1.918481	-1.550627
40	1	0	3.014319	-2.319214	-2.538435
41	6	0	1.892944	3.743448	1.497610
42	1	0	2.211202	4.256867	2.401692
43	6	0	2.381499	4.134371	0.257780
44	1	0	3.088236	4.955339	0.170265
45	6	0	1.939406	3.465453	-0.877253
46	1	0	2.304693	3.774404	-1.854749
47	6	0	5.249405	-2.137258	-0.989510
48	1	0	5.292084	-3.062988	-1.572086
49	1	0	5.717460	-1.353981	-1.597620
50	1	0	5.866773	-2.269994	-0.096535
51	1	0	-4.003695	3.622153	-1.223846
52	1	0	-1.390438	-4.956289	1.075239
53	6	0	0.625140	1.744721	-2.097145
54	1	0	-0.415967	1.418859	-2.075659
55	1	0	1.238415	0.859734	-2.293756
56	1	0	0.755730	2.428334	-2.942572
57	9	0	-0.865267	0.791275	2.148150

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 3.8748 eV 319.97 nm f=0.2490
<S**2>=0.000
108 ->109 0.68077

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)

SCF Done: E(RCAM-B3LYP) = -1261.72624969 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.58412122 a.u.

Excited State 1: Singlet-A 3.8679 eV 320.54 nm f=0.1858
<S**2>=0.000
108 ->109 0.68040

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.50134629 a.u.
Lowest frequency = 29.1480

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.176031	-0.630809	0.384465
2	5	0	-0.589519	0.879991	0.712288
3	6	0	-2.001871	1.162968	-0.006560
4	6	0	-2.424639	2.440421	-0.324276
5	1	0	-1.725178	3.264224	-0.195060
6	6	0	-3.715033	2.716363	-0.813657
7	6	0	-4.606436	1.652644	-0.972988
8	1	0	-5.609278	1.837608	-1.353019
9	6	0	-4.231956	0.359846	-0.660525
10	1	0	-4.951142	-0.438090	-0.809922
11	6	0	-2.917226	0.067711	-0.164760
12	6	0	-2.530012	-1.252416	0.203772
13	6	0	-3.444863	-2.355645	0.221252
14	1	0	-4.489337	-2.177089	-0.001092
15	6	0	-0.770957	-2.921886	0.806479
16	1	0	0.264793	-3.120079	1.057389
17	6	0	-3.050750	-3.641397	0.530092
18	1	0	-3.796630	-4.432412	0.540779
19	6	0	-1.709528	-3.950347	0.838619
20	6	0	-1.131264	-1.598701	0.491308
21	6	0	1.066914	2.317942	-0.874666
22	6	0	0.575951	1.971972	0.402671
23	6	0	1.071535	2.708857	1.488219
24	1	0	0.689476	2.474363	2.476226
25	6	0	2.192944	-0.893116	1.021890
26	6	0	1.964258	-0.435554	2.440457
27	1	0	2.271240	-1.221769	3.140236
28	1	0	2.567622	0.449664	2.665981
29	1	0	0.923487	-0.183179	2.632430
30	6	0	1.419475	-1.626948	-1.175955
31	6	0	1.151886	-1.051267	0.090500
32	6	0	0.329771	-1.902971	-2.179839
33	1	0	0.743959	-1.942789	-3.190787
34	1	0	-0.152009	-2.865184	-1.975462
35	1	0	-0.453255	-1.142767	-2.155070
36	6	0	3.488890	-1.255248	0.646697

37	1	0	4.287894	-1.135750	1.375648
38	6	0	3.786828	-1.772538	-0.605767
39	6	0	2.727977	-1.956826	-1.499655
40	1	0	2.930114	-2.375714	-2.482979
41	6	0	2.018393	3.719181	1.352349
42	1	0	2.370616	4.260179	2.226981
43	6	0	2.501507	4.034208	0.088426
44	1	0	3.238086	4.821946	-0.045083
45	6	0	2.016727	3.335300	-1.010235
46	1	0	2.378114	3.586823	-2.005414
47	6	0	5.196347	-2.130841	-0.996576
48	1	0	5.254834	-3.149676	-1.394067
49	1	0	5.575135	-1.461541	-1.777711
50	1	0	5.875598	-2.061670	-0.142748
51	1	0	-4.007555	3.730770	-1.069812
52	1	0	-1.417402	-4.958852	1.109326
53	6	0	0.611708	1.615450	-2.131292
54	1	0	-0.407515	1.238620	-2.032103
55	1	0	1.260063	0.763897	-2.364552
56	1	0	0.644105	2.292757	-2.991209
57	9	0	-0.845054	0.868716	2.141391

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.59616051 a.u.

Excited State 1: Singlet-A 3.2961 eV 376.15 nm f=0.2327
<S**2>=0.000
108 ->109 0.69006

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.71477746 a.u.

Results

Absorb Energy =	0.142 a.u.	3.868 eV	320.579 nm
Emission Energy =	0.119 a.u.	3.228 eV	384.122 nm
Stokes Shift =	0.024 a.u.	0.640 eV	63.543 nm

5.1.8 Compound 4 – GS2-0-R

<u>*n*-hexane</u>

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : n-Hexane
SCF Done: E(RCAM-B3LYP) = -1261.59974138 a.u.
Lowest frequency = 22.0372

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.006676	-0.647370	-0.070609
2	5	0	0.602712	0.672916	-0.655955
3	6	0	2.211005	0.557408	-0.673531
4	6	0	2.937352	1.597742	-1.267749
5	1	0	2.387864	2.460316	-1.637591
6	6	0	4.316627	1.568305	-1.393754
7	6	0	5.012292	0.459317	-0.915734
8	1	0	6.094272	0.404273	-1.008616
9	6	0	4.320145	-0.584641	-0.327399
10	1	0	4.889117	-1.442766	0.013116
11	6	0	2.919008	-0.554797	-0.191438
12	6	0	2.177034	-1.684536	0.415810
13	6	0	2.850750	-2.768290	0.986691
14	1	0	3.934234	-2.749004	1.023062
15	6	0	0.110212	-2.851807	0.934471
16	1	0	-0.971606	-2.894709	0.921257
17	6	0	2.206645	-3.877145	1.515173
18	1	0	2.778616	-4.693232	1.946199
19	6	0	0.817824	-3.911797	1.471245
20	6	0	0.748283	-1.701876	0.409953
21	6	0	0.804196	2.335153	1.345519
22	6	0	0.103838	2.000335	0.178632
23	6	0	-0.981686	2.835608	-0.168020
24	6	0	-1.997329	-1.348332	-1.298533
25	6	0	-1.139472	-1.838108	-2.434699
26	1	0	-0.425884	-2.593434	-2.088851
27	1	0	-1.756210	-2.283815	-3.221453
28	1	0	-0.558943	-1.012295	-2.847369
29	6	0	-2.234235	-0.450346	0.945522
30	6	0	-1.414729	-0.808589	-0.136317
31	6	0	-1.658532	0.028223	2.252857
32	1	0	-2.374285	-0.137349	3.064621
33	1	0	-0.732874	-0.498309	2.495900
34	1	0	-1.420726	1.094164	2.219354
35	6	0	-3.383654	-1.453256	-1.380751
36	1	0	-3.824547	-1.867495	-2.285523
37	6	0	-4.216562	-1.055069	-0.338009
38	6	0	-3.619136	-0.574235	0.820475
39	1	0	-4.245801	-0.291829	1.664426
40	6	0	-1.320101	3.916539	0.652584
41	1	0	-2.163548	4.544829	0.371049
42	6	0	-0.611681	4.211709	1.811439
43	1	0	-0.899862	5.059511	2.428443
44	6	0	0.467860	3.410983	2.160211
45	1	0	1.044216	3.621793	3.058123
46	6	0	-5.716222	-1.141919	-0.464854
47	1	0	-6.196182	-1.217266	0.515725
48	1	0	-6.127625	-0.254253	-0.960883
49	1	0	-6.018874	-2.011302	-1.057403
50	1	0	4.848900	2.393675	-1.860199
51	1	0	0.273830	-4.766862	1.865604
52	9	0	0.160030	0.812102	-2.024737
53	6	0	-1.811618	2.617440	-1.414345
54	1	0	-1.209209	2.736932	-2.317455
55	1	0	-2.223602	1.606542	-1.454549
56	1	0	-2.642603	3.330833	-1.450310
57	1	0	1.652097	1.715034	1.627303

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 3.7559 eV 330.11 nm f=0.2609
<S**2>=0.000
108 ->109 0.68549

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.68973333 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.55197591 a.u.

Excited State 1: Singlet-A 3.7564 eV 330.06 nm f=0.1952
<S**2>=0.000
108 ->109 0.68626

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.46796627 a.u.
Lowest frequency = 22.6812

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.239173	-0.570988	-0.006947
2	5	0	0.541833	0.566470	-0.776340
3	6	0	2.000159	0.037522	-1.141116
4	6	0	2.736569	0.650953	-2.141238
5	1	0	2.264518	1.448916	-2.712011
6	6	0	4.050906	0.273812	-2.440719
7	6	0	4.643520	-0.740018	-1.677147
8	1	0	5.669663	-1.040540	-1.882293
9	6	0	3.945768	-1.375115	-0.672027
10	1	0	4.439952	-2.165606	-0.117601
11	6	0	2.586821	-1.021190	-0.377549
12	6	0	1.825388	-1.704514	0.618873
13	6	0	2.394157	-2.705213	1.469493
14	1	0	3.464306	-2.867087	1.441661
15	6	0	-0.367241	-2.328106	1.635797
16	1	0	-1.436002	-2.167581	1.706108
17	6	0	1.632627	-3.473213	2.329294
18	1	0	2.126889	-4.220450	2.946411
19	6	0	0.239279	-3.313928	2.416193
20	6	0	0.376127	-1.513017	0.763065
21	6	0	1.452098	1.778253	1.369028
22	6	0	0.645580	1.876771	0.227138
23	6	0	-0.017344	3.105870	0.011000

24	6	0	-2.202900	-1.298869	-1.228026
25	6	0	-1.300078	-2.037311	-2.178680
26	1	0	-0.682750	-2.772536	-1.653110
27	1	0	-1.885896	-2.562265	-2.938811
28	1	0	-0.622685	-1.338167	-2.675155
29	6	0	-2.501932	0.079090	0.759595
30	6	0	-1.665917	-0.594474	-0.136764
31	6	0	-1.978010	0.813525	1.967259
32	1	0	-2.712412	0.775414	2.778238
33	1	0	-1.042777	0.384746	2.327930
34	1	0	-1.779091	1.865586	1.741202
35	6	0	-3.579064	-1.296635	-1.415836
36	1	0	-3.992236	-1.839424	-2.263463
37	6	0	-4.438881	-0.616980	-0.552576
38	6	0	-3.881402	0.051107	0.527755
39	1	0	-4.533726	0.570751	1.226637
40	6	0	0.157690	4.152236	0.924123
41	1	0	-0.357361	5.093741	0.741159
42	6	0	0.961769	4.025882	2.049500
43	1	0	1.073476	4.857950	2.740189
44	6	0	1.616730	2.820424	2.271905
45	1	0	2.256246	2.691793	3.141802
46	6	0	-5.925993	-0.606273	-0.797820
47	1	0	-6.472466	-0.252569	0.081198
48	1	0	-6.186738	0.052709	-1.634557
49	1	0	-6.298781	-1.605209	-1.047483
50	1	0	4.601409	0.757035	-3.243383
51	1	0	-0.354138	-3.928925	3.084213
52	9	0	-0.209318	0.877945	-1.939292
53	6	0	-0.931859	3.360133	-1.168144
54	1	0	-0.404775	3.262896	-2.119948
55	1	0	-1.756731	2.644195	-1.204076
56	1	0	-1.353653	4.369325	-1.107318
57	1	0	1.977275	0.844027	1.552169

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.56257914 a.u.

Excited State 1: Singlet-A 3.1943 eV 388.14 nm f=0.1823
<S**2>=0.000
108 ->109 0.69373

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.67972218 a.u.

Results

Absorb Energy =	0.138 a.u.	3.749 eV	330.751 nm
Emission Energy =	0.117 a.u.	3.188 eV	388.955 nm
Stokes Shift =	0.021 a.u.	0.561 eV	58.204 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1261.62687915 a.u.
Lowest frequency = 15.0220

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.008373	-0.646043	-0.072928
2	5	0	0.605522	0.673371	-0.652830
3	6	0	2.214495	0.559849	-0.668884
4	6	0	2.943843	1.603259	-1.255465
5	1	0	2.398158	2.471947	-1.617443
6	6	0	4.323389	1.571371	-1.384163
7	6	0	5.016283	0.454407	-0.919559
8	1	0	6.097438	0.397161	-1.015345
9	6	0	4.321967	-0.593030	-0.338871
10	1	0	4.889482	-1.455600	-0.007757
11	6	0	2.920921	-0.558435	-0.196920
12	6	0	2.177751	-1.685593	0.413417
13	6	0	2.852243	-2.767705	0.989167
14	1	0	3.935654	-2.749908	1.024865
15	6	0	0.110176	-2.845922	0.944185
16	1	0	-0.971804	-2.887233	0.934423
17	6	0	2.206999	-3.871998	1.525681
18	1	0	2.777951	-4.686384	1.960518
19	6	0	0.817223	-3.904154	1.485912
20	6	0	0.749271	-1.700062	0.411216
21	6	0	0.803996	2.346874	1.339043
22	6	0	0.102032	2.002104	0.175367
23	6	0	-0.989294	2.830377	-0.171267
24	6	0	-1.996082	-1.354844	-1.296432
25	6	0	-1.137880	-1.858645	-2.426742
26	1	0	-0.468776	-2.655543	-2.084077
27	1	0	-1.757148	-2.259744	-3.234544
28	1	0	-0.512303	-1.052973	-2.811529
29	6	0	-2.234157	-0.445592	0.942942
30	6	0	-1.414314	-0.807688	-0.137429
31	6	0	-1.660421	0.037933	2.249561
32	1	0	-2.378216	-0.120461	3.060332
33	1	0	-0.737410	-0.491043	2.497722
34	1	0	-1.418115	1.102676	2.211491
35	6	0	-3.382620	-1.460417	-1.379538
36	1	0	-3.822981	-1.879819	-2.281929
37	6	0	-4.216886	-1.057403	-0.339012
38	6	0	-3.619251	-0.571659	0.818214
39	1	0	-4.246587	-0.288708	1.661153
40	6	0	-1.329048	3.915856	0.643678
41	1	0	-2.175764	4.539038	0.361768
42	6	0	-0.617407	4.221566	1.798226
43	1	0	-0.905753	5.072332	2.410324
44	6	0	0.466313	3.426590	2.148676
45	1	0	1.044260	3.644732	3.043564
46	6	0	-5.716276	-1.147344	-0.465516

47	1	0	-6.195993	-1.222357	0.514802
48	1	0	-6.128065	-0.260483	-0.962039
49	1	0	-6.016765	-2.016730	-1.058382
50	1	0	4.857450	2.399469	-1.843016
51	1	0	0.273051	-4.755606	1.886909
52	9	0	0.170832	0.811745	-2.029549
53	6	0	-1.827623	2.601842	-1.410411
54	1	0	-1.239741	2.742870	-2.320574
55	1	0	-2.217640	1.582593	-1.452473
56	1	0	-2.673209	3.297606	-1.433426
57	1	0	1.655246	1.732696	1.624795

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 3.7678 eV 329.06 nm f=0.2639
<S**2>=0.000
108 ->109 0.68746

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.71679976 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.57844353 a.u.

Excited State 1: Singlet-A 3.7668 eV 329.15 nm f=0.1944
<S**2>=0.000
108 ->109 0.68678

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.49692609 a.u.
Lowest frequency = 16.6044

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.227458	-0.582678	-0.027450
2	5	0	0.550376	0.573070	-0.775946
3	6	0	2.020715	0.065208	-1.126452
4	6	0	2.761701	0.689072	-2.115610
5	1	0	2.287987	1.482317	-2.691931
6	6	0	4.087578	0.331901	-2.399837
7	6	0	4.684266	-0.676821	-1.631768
8	1	0	5.716842	-0.962064	-1.824582
9	6	0	3.982585	-1.325952	-0.637898
10	1	0	4.479565	-2.113092	-0.081596
11	6	0	2.611801	-0.992555	-0.360532
12	6	0	1.845765	-1.694429	0.613701

13	6	0	2.420108	-2.690194	1.470776
14	1	0	3.495132	-2.818978	1.475922
15	6	0	-0.356986	-2.385155	1.566448
16	1	0	-1.430221	-2.250653	1.616449
17	6	0	1.655460	-3.493745	2.292511
18	1	0	2.149928	-4.237285	2.913186
19	6	0	0.254295	-3.370970	2.340401
20	6	0	0.387410	-1.531283	0.727632
21	6	0	1.426902	1.795019	1.374262
22	6	0	0.620436	1.880843	0.230724
23	6	0	-0.069498	3.096303	0.021306
24	6	0	-2.201137	-1.276375	-1.258656
25	6	0	-1.307495	-1.981363	-2.243617
26	1	0	-0.662568	-2.712744	-1.746758
27	1	0	-1.900660	-2.505663	-2.997671
28	1	0	-0.657602	-1.259315	-2.743905
29	6	0	-2.488716	0.036361	0.774506
30	6	0	-1.657413	-0.603100	-0.151260
31	6	0	-1.959481	0.734702	2.001426
32	1	0	-2.698808	0.690225	2.806767
33	1	0	-1.033419	0.282063	2.357780
34	1	0	-1.744142	1.788197	1.799396
35	6	0	-3.579844	-1.277121	-1.432694
36	1	0	-3.998595	-1.798067	-2.290846
37	6	0	-4.435355	-0.630331	-0.540303
38	6	0	-3.870034	0.008108	0.555089
39	1	0	-4.518502	0.499958	1.276713
40	6	0	0.078418	4.140969	0.941945
41	1	0	-0.458766	5.070817	0.765351
42	6	0	0.882069	4.025666	2.069060
43	1	0	0.972205	4.854977	2.765510
44	6	0	1.564969	2.834264	2.285601
45	1	0	2.203955	2.715306	3.157080
46	6	0	-5.925103	-0.624602	-0.767842
47	1	0	-6.464042	-0.306183	0.128659
48	1	0	-6.199803	0.060050	-1.578666
49	1	0	-6.290523	-1.617493	-1.048736
50	1	0	4.641187	0.825155	-3.193965
51	1	0	-0.339947	-4.013551	2.981066
52	9	0	-0.184760	0.880755	-1.953436
53	6	0	-0.988282	3.338589	-1.157163
54	1	0	-0.456529	3.272990	-2.109243
55	1	0	-1.790183	2.597874	-1.203864
56	1	0	-1.441693	4.332455	-1.084563
57	1	0	1.971559	0.871246	1.554736

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.59113862 a.u.

Excited State 1: Singlet-A 3.1612 eV 392.20 nm f=0.1902
<S**2>=0.000
108 ->109 0.69444

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.70574324 a.u.

Results

Absorb Energy =	0.138 a.u.	3.765 eV	329.319 nm
Emission Energy =	0.115 a.u.	3.119 eV	397.570 nm
Stokes Shift =	0.024 a.u.	0.646 eV	68.251 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1261.63580276 a.u.
Lowest frequency = 5.6699

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.027138	-0.656980	-0.086060
2	5	0	0.610225	0.678371	-0.641027
3	6	0	2.222269	0.607377	-0.602784
4	6	0	2.944787	1.697399	-1.109645
5	1	0	2.390412	2.571573	-1.444199
6	6	0	4.327973	1.705552	-1.194322
7	6	0	5.034037	0.583489	-0.762349
8	1	0	6.118865	0.558605	-0.820880
9	6	0	4.348363	-0.508959	-0.259818
10	1	0	4.928930	-1.369643	0.052321
11	6	0	2.942143	-0.517917	-0.168040
12	6	0	2.209264	-1.694287	0.356298
13	6	0	2.895019	-2.804548	0.863225
14	1	0	3.978028	-2.780594	0.898994
15	6	0	0.154660	-2.908857	0.808396
16	1	0	-0.926666	-2.963428	0.790194
17	6	0	2.261360	-3.945943	1.330379
18	1	0	2.840736	-4.779849	1.713662
19	6	0	0.871714	-3.989620	1.288880
20	6	0	0.781610	-1.726563	0.344364
21	6	0	0.720301	2.394797	1.326893
22	6	0	0.047004	2.002756	0.159994
23	6	0	-1.054158	2.800921	-0.226588
24	6	0	-2.014666	-1.315635	-1.287942
25	6	0	-1.198005	-1.781232	-2.465081
26	1	0	-0.527356	-2.597508	-2.173865
27	1	0	-1.847069	-2.147533	-3.265695
28	1	0	-0.575950	-0.969729	-2.842177
29	6	0	-2.181745	-0.530885	1.003850
30	6	0	-1.397101	-0.825713	-0.123360
31	6	0	-1.552204	-0.160479	2.321053
32	1	0	-2.316888	-0.058937	3.096519
33	1	0	-0.844724	-0.931973	2.643126
34	1	0	-0.996508	0.776361	2.256111
35	6	0	-3.405057	-1.414909	-1.331781
36	1	0	-3.874491	-1.789508	-2.239030

37	6	0	-4.205334	-1.062729	-0.248164
38	6	0	-3.569656	-0.643777	0.916719
39	1	0	-4.169228	-0.407981	1.793409
40	6	0	-1.424513	3.905950	0.548471
41	1	0	-2.276091	4.505699	0.233223
42	6	0	-0.737756	4.259971	1.704037
43	1	0	-1.049337	5.124904	2.283612
44	6	0	0.350742	3.492730	2.098145
45	1	0	0.909823	3.746986	2.995279
46	6	0	-5.708347	-1.137761	-0.332551
47	1	0	-6.154498	-1.332306	0.647164
48	1	0	-6.133441	-0.196444	-0.700943
49	1	0	-6.031452	-1.927595	-1.017130
50	1	0	4.855030	2.568629	-1.592443
51	1	0	0.336162	-4.869116	1.636984
52	9	0	0.228592	0.813805	-2.038150
53	6	0	-1.872760	2.520351	-1.468106
54	1	0	-1.275157	2.633702	-2.375411
55	1	0	-2.251892	1.495960	-1.476411
56	1	0	-2.725265	3.205010	-1.527182
57	1	0	1.579944	1.808586	1.644617

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 3.8053 eV 325.82 nm f=0.2620
<S**2>=0.000
108 ->109 0.68689

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.72542823 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.58537186 a.u.

Excited State 1: Singlet-A 3.8041 eV 325.92 nm f=0.1993
<S**2>=0.000
108 ->109 0.68612

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.50643795 a.u.
Lowest frequency = 16.6914

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.232764	-0.581372	-0.023362

2	5	0	0.548649	0.570722	-0.772468
3	6	0	2.017503	0.057068	-1.125876
4	6	0	2.762852	0.680179	-2.112232
5	1	0	2.295704	1.479454	-2.685992
6	6	0	4.087519	0.317055	-2.398246
7	6	0	4.678548	-0.698478	-1.634181
8	1	0	5.709290	-0.988845	-1.828297
9	6	0	3.973557	-1.347053	-0.642233
10	1	0	4.467065	-2.137754	-0.088108
11	6	0	2.603554	-1.007222	-0.362847
12	6	0	1.835940	-1.706480	0.610327
13	6	0	2.406183	-2.709594	1.463064
14	1	0	3.479809	-2.849356	1.462179
15	6	0	-0.368849	-2.380453	1.572979
16	1	0	-1.440590	-2.236719	1.628476
17	6	0	1.638762	-3.506238	2.288282
18	1	0	2.129239	-4.254604	2.905990
19	6	0	0.238262	-3.370143	2.344076
20	6	0	0.378189	-1.532269	0.729508
21	6	0	1.434177	1.788354	1.375121
22	6	0	0.629538	1.880157	0.230389
23	6	0	-0.044786	3.103678	0.016745
24	6	0	-2.210016	-1.278372	-1.248818
25	6	0	-1.320258	-2.001355	-2.224629
26	1	0	-0.689165	-2.739494	-1.719609
27	1	0	-1.916130	-2.522250	-2.978585
28	1	0	-0.657341	-1.292678	-2.727129
29	6	0	-2.492366	0.055851	0.771059
30	6	0	-1.663586	-0.596692	-0.147384
31	6	0	-1.962315	0.760985	1.993602
32	1	0	-2.698224	0.715321	2.801788
33	1	0	-1.032119	0.314984	2.347427
34	1	0	-1.754733	1.815123	1.786925
35	6	0	-3.588276	-1.272262	-1.425309
36	1	0	-4.009200	-1.799245	-2.278599
37	6	0	-4.441548	-0.611244	-0.540263
38	6	0	-3.873815	0.034109	0.549712
39	1	0	-4.520227	0.536224	1.265902
40	6	0	0.117500	4.150242	0.933190
41	1	0	-0.407767	5.086145	0.753720
42	6	0	0.920686	4.029299	2.060225
43	1	0	1.022393	4.860351	2.752726
44	6	0	1.587066	2.829387	2.282376
45	1	0	2.223808	2.705488	3.154740
46	6	0	-5.931146	-0.603187	-0.768001
47	1	0	-6.464915	-0.212459	0.102360
48	1	0	-6.197221	0.021530	-1.628259
49	1	0	-6.309075	-1.609692	-0.974253
50	1	0	4.643547	0.809927	-3.190773
51	1	0	-0.357576	-4.006968	2.988892
52	9	0	-0.186967	0.877823	-1.950707
53	6	0	-0.962880	3.353094	-1.160892
54	1	0	-0.434199	3.282802	-2.114524
55	1	0	-1.771490	2.619559	-1.204740
56	1	0	-1.407500	4.350660	-1.088866
57	1	0	1.965441	0.857596	1.560393

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)

```
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
 After PCM corrections, the energy is -1261.60080008 a.u.

 Excited State   1:      Singlet-A      3.1424 eV  394.55 nm  f=0.1914
<S**2>=0.000
     108 ->109         0.69460

Step7

  Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

 SCF Done: E(RCAM-B3LYP) = -1261.71404880 a.u.

                              Results
 ---------------------------------------------------------------------
     Absorb Energy     =  | 0.140 a.u. | 3.811 eV | 325.321 nm
 ------------------------|------------|----------|----------------
     Emission Energy   =  | 0.113 a.u. | 3.082 eV | 402.330 nm
 ------------------------|------------|----------|----------------
     Stokes Shift      =  | 0.027 a.u. | 0.729 eV | 77.008 nm
 ---------------------------------------------------------------------
```

5.1.9 Compound 4 – GS2-180-R

<u>*n*-hexane</u>

```
Step1

 Method: cam-b3lyp/6-31G(d)
 Solvent : n-Hexane
 SCF Done: E(RCAM-B3LYP) = -1261.60088917 a.u.
 Lowest frequency =  14.8094

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          7           0       -0.194475   -0.583748   -0.069121
      2          5           0        0.542322    0.626148   -0.733735
      3          6           0        2.113198    0.286693   -0.851339
      4          6           0        2.925821    1.157816   -1.586618
      5          1           0        2.473915    2.057918   -1.997288
      6          6           0        4.272704    0.911555   -1.806218
      7          6           0        4.836538   -0.256074   -1.296779
      8          1           0        5.885563   -0.483472   -1.470656
      9          6           0        4.052994   -1.138591   -0.571958
     10          1           0        4.510803   -2.055293   -0.215590
     11          6           0        2.692904   -0.879165   -0.325510
     12          6           0        1.856339   -1.821559    0.452878
     13          6           0        2.428072   -2.896620    1.139594
     14          1           0        3.508972   -2.985294    1.158825
     15          6           0       -0.307699   -2.681998    1.144069
     16          1           0       -1.388258   -2.606853    1.150026
     17          6           0        1.683771   -3.858611    1.806431
     18          1           0        2.176440   -4.674837    2.326029
     19          6           0        0.297984   -3.747926    1.784449
     20          6           0        0.436183   -1.670354    0.490782
     21          6           0       -0.569269    2.994014   -0.637921
     22          6           0        0.250509    2.063737    0.011006
```

23	6	0	0.791396	2.454526	1.256320
24	6	0	-2.199988	-1.193435	-1.340776
25	6	0	-1.343656	-1.839536	-2.396974
26	1	0	-0.767945	-2.673027	-1.979895
27	1	0	-1.962208	-2.228411	-3.211978
28	1	0	-0.630408	-1.115809	-2.791996
29	6	0	-2.451602	-0.125690	0.824532
30	6	0	-1.621680	-0.626002	-0.190350
31	6	0	-1.883677	0.378551	2.124311
32	1	0	-1.368311	1.332165	1.994359
33	1	0	-2.680495	0.516374	2.861953
34	1	0	-1.156298	-0.328307	2.534505
35	6	0	-3.585450	-1.185383	-1.481590
36	1	0	-4.022094	-1.619763	-2.379039
37	6	0	-4.423249	-0.647190	-0.509131
38	6	0	-3.835453	-0.141324	0.643904
39	1	0	-4.469389	0.250654	1.436991
40	6	0	0.497131	3.711045	1.789149
41	1	0	0.922142	3.987951	2.752587
42	6	0	-0.327682	4.610873	1.121372
43	1	0	-0.544625	5.582781	1.558196
44	6	0	-0.865903	4.245789	-0.104297
45	1	0	-1.515361	4.930652	-0.645457
46	6	0	-5.917781	-0.611856	-0.703668
47	1	0	-6.268625	-1.478920	-1.272611
48	1	0	-6.445845	-0.600900	0.254978
49	1	0	-6.228347	0.283810	-1.255619
50	1	0	4.878003	1.610657	-2.378198
51	1	0	-0.322900	-4.489498	2.281582
52	9	0	0.028780	0.773905	-2.077974
53	6	0	1.694618	1.537004	2.046319
54	1	0	1.830290	1.905463	3.068994
55	1	0	1.291865	0.522560	2.099701
56	1	0	2.683302	1.454880	1.583375
57	1	0	-0.981922	2.713151	-1.601410

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=n-hexane)

Excited State 1: Singlet-A 3.7272 eV 332.65 nm f=0.2466
<S**2>=0.000
108 ->109 0.68461

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.69122173 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.55447516 a.u.

Excited State 1: Singlet-A 3.7268 eV 332.68 nm f=0.1848
<S**2>=0.000
108 ->109 0.68575

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.46831459 a.u.
Lowest frequency = -5.5510

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.219521	-0.568888	-0.045223
2	5	0	0.533327	0.596408	-0.810129
3	6	0	2.059737	0.198620	-1.025796
4	6	0	2.845349	0.960124	-1.875912
5	1	0	2.385873	1.813558	-2.372281
6	6	0	4.193898	0.668454	-2.116275
7	6	0	4.765121	-0.424782	-1.454406
8	1	0	5.812910	-0.669803	-1.620314
9	6	0	4.021395	-1.203164	-0.592589
10	1	0	4.501495	-2.050035	-0.114986
11	6	0	2.633122	-0.927539	-0.354605
12	6	0	1.850245	-1.724357	0.531330
13	6	0	2.414698	-2.785682	1.310241
14	1	0	3.487395	-2.928758	1.299725
15	6	0	-0.355200	-2.454022	1.445481
16	1	0	-1.425911	-2.307886	1.512213
17	6	0	1.643900	-3.635203	2.081241
18	1	0	2.134416	-4.426178	2.644643
19	6	0	0.248000	-3.495965	2.153618
20	6	0	0.395725	-1.563897	0.654157
21	6	0	-0.582211	2.922847	-0.572183
22	6	0	0.325812	2.019806	-0.003857
23	6	0	0.973440	2.423920	1.184740
24	6	0	-2.188446	-1.317152	-1.264821
25	6	0	-1.296092	-2.057383	-2.224292
26	1	0	-0.644716	-2.760159	-1.695784
27	1	0	-1.891901	-2.619353	-2.949225
28	1	0	-0.653417	-1.353968	-2.757815
29	6	0	-2.485909	0.037741	0.738134
30	6	0	-1.648595	-0.609163	-0.176088
31	6	0	-1.964054	0.746290	1.961400
32	1	0	-1.845316	1.818228	1.779118
33	1	0	-2.663345	0.619952	2.794576
34	1	0	-0.992940	0.357047	2.268636
35	6	0	-3.566618	-1.327368	-1.438705
36	1	0	-3.982073	-1.872451	-2.283750
37	6	0	-4.426518	-0.664365	-0.563002
38	6	0	-3.866852	-0.003231	0.519994
39	1	0	-4.518096	0.498023	1.233192
40	6	0	0.685385	3.669233	1.745645
41	1	0	1.192952	3.959570	2.663581
42	6	0	-0.226634	4.543846	1.163934
43	1	0	-0.430856	5.507982	1.622896
44	6	0	-0.863167	4.164722	-0.009856
45	1	0	-1.576116	4.831190	-0.490059
46	6	0	-5.915701	-0.668297	-0.795233
47	1	0	-6.275236	-1.663653	-1.076511
48	1	0	-6.459797	-0.353727	0.100050
49	1	0	-6.194013	0.015411	-1.606120

50	1	0	4.784001	1.275026	-2.797801
51	1	0	-0.351391	-4.168682	2.757628
52	9	0	-0.135808	0.730811	-2.067533
53	6	0	1.993194	1.555366	1.876572
54	1	0	2.293428	1.993786	2.833969
55	1	0	1.618732	0.545757	2.068047
56	1	0	2.888043	1.434796	1.258537
57	1	0	-1.079972	2.630819	-1.490370

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=n-hexane,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.56360749 a.u.

Excited State 1: Singlet-A 3.2444 eV 382.15 nm f=0.2030
<S**2>=0.000
108 ->109 0.69328

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=n-hexane, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.68275049 a.u.

Results

Absorb Energy =	0.137 a.u.	3.721 eV	333.196 nm
Emission Energy =	0.119 a.u.	3.242 eV	382.426 nm
Stokes Shift =	0.018 a.u.	0.479 eV	49.230 nm

THF

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : TetraHydroFuran
SCF Done: E(RCAM-B3LYP) = -1261.62831999 a.u.
Lowest frequency = 15.9562

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.197621	-0.583009	-0.069844
2	5	0	0.546960	0.621124	-0.728477
3	6	0	2.117957	0.279027	-0.837851
4	6	0	2.941798	1.158728	-1.551040
5	1	0	2.499185	2.068496	-1.951245
6	6	0	4.291091	0.913772	-1.759712
7	6	0	4.847434	-0.261027	-1.257604
8	1	0	5.898006	-0.486978	-1.420602
9	6	0	4.053759	-1.152733	-0.554494
10	1	0	4.509283	-2.071718	-0.201952
11	6	0	2.690221	-0.895277	-0.321131
12	6	0	1.843373	-1.846033	0.436480

13	6	0	2.405710	-2.939412	1.104043
14	1	0	3.485023	-3.043717	1.117911
15	6	0	-0.328375	-2.695068	1.117346
16	1	0	-1.407910	-2.608155	1.129090
17	6	0	1.651989	-3.903436	1.757163
18	1	0	2.136362	-4.734069	2.260849
19	6	0	0.266854	-3.776803	1.741479
20	6	0	0.424912	-1.682300	0.476275
21	6	0	-0.526831	3.011422	-0.659586
22	6	0	0.261843	2.064977	0.005012
23	6	0	0.789837	2.448655	1.258695
24	6	0	-2.213552	-1.179966	-1.334505
25	6	0	-1.367960	-1.841907	-2.390230
26	1	0	-0.801450	-2.680094	-1.969546
27	1	0	-1.992712	-2.229007	-3.200610
28	1	0	-0.647060	-1.131179	-2.794333
29	6	0	-2.449917	-0.109334	0.830940
30	6	0	-1.626646	-0.614625	-0.187161
31	6	0	-1.876907	0.382033	2.133699
32	1	0	-1.349068	1.329526	2.009718
33	1	0	-2.671831	0.524837	2.871665
34	1	0	-1.157782	-0.335030	2.540829
35	6	0	-3.599775	-1.160803	-1.471984
36	1	0	-4.042982	-1.594838	-2.366041
37	6	0	-4.431069	-0.613225	-0.498071
38	6	0	-3.834677	-0.111456	0.653222
39	1	0	-4.463462	0.283677	1.448436
40	6	0	0.512869	3.712753	1.783576
41	1	0	0.926794	3.984028	2.753071
42	6	0	-0.280806	4.628708	1.099085
43	1	0	-0.483823	5.606029	1.529392
44	6	0	-0.806020	4.271845	-0.135056
45	1	0	-1.429629	4.969417	-0.689396
46	6	0	-5.925798	-0.567369	-0.687147
47	1	0	-6.285204	-1.435111	-1.248773
48	1	0	-6.449499	-0.543522	0.273094
49	1	0	-6.229322	0.326566	-1.245185
50	1	0	4.903964	1.620205	-2.313730
51	1	0	-0.360472	-4.519033	2.228756
52	9	0	0.040665	0.767961	-2.081590
53	6	0	1.660342	1.515056	2.066659
54	1	0	1.775462	1.876638	3.093809
55	1	0	1.241501	0.506440	2.102757
56	1	0	2.659657	1.422512	1.629226
57	1	0	-0.930425	2.740662	-1.630189

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(solvent=THF)

Excited State 1: Singlet-A 3.7464 eV 330.95 nm f=0.2518
<S**2>=0.000
108 ->109 0.68787

Step3

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.71867422 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.58084312 a.u.

Excited State 1: Singlet-A 3.7452 eV 331.05 nm f=0.1857
<S**2>=0.000
108 ->109 0.68738

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.49727329 a.u.
Lowest frequency = 21.5182

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.214506	-0.575376	-0.054550
2	5	0	0.534986	0.598340	-0.808097
3	6	0	2.067495	0.212835	-1.016469
4	6	0	2.856243	0.981498	-1.856271
5	1	0	2.397760	1.831166	-2.360439
6	6	0	4.212711	0.705760	-2.082084
7	6	0	4.789623	-0.379098	-1.410351
8	1	0	5.843173	-0.608501	-1.559156
9	6	0	4.043678	-1.169368	-0.561497
10	1	0	4.532633	-2.003542	-0.071418
11	6	0	2.644750	-0.914426	-0.343834
12	6	0	1.858985	-1.731311	0.514872
13	6	0	2.420740	-2.813712	1.271520
14	1	0	3.491903	-2.966441	1.253285
15	6	0	-0.349868	-2.475288	1.415614
16	1	0	-1.420463	-2.330215	1.483832
17	6	0	1.649123	-3.670879	2.030396
18	1	0	2.136155	-4.473849	2.578718
19	6	0	0.251911	-3.525303	2.108785
20	6	0	0.400796	-1.573361	0.633185
21	6	0	-0.586437	2.925623	-0.580952
22	6	0	0.314428	2.019733	-0.005915
23	6	0	0.948895	2.421233	1.191054
24	6	0	-2.194062	-1.314152	-1.268300
25	6	0	-1.312481	-2.060433	-2.234029
26	1	0	-0.679814	-2.785324	-1.712071
27	1	0	-1.916343	-2.601284	-2.967611
28	1	0	-0.652793	-1.366452	-2.758613
29	6	0	-2.477588	0.029230	0.744489
30	6	0	-1.646273	-0.612556	-0.179014
31	6	0	-1.950947	0.723370	1.974038
32	1	0	-1.829773	1.796693	1.802871
33	1	0	-2.649445	0.591882	2.806341
34	1	0	-0.980059	0.329173	2.276457
35	6	0	-3.573547	-1.318872	-1.435846
36	1	0	-3.995215	-1.859080	-2.280562
37	6	0	-4.427665	-0.657267	-0.552608
38	6	0	-3.859796	-0.005349	0.532551
39	1	0	-4.506167	0.490635	1.253373

40	6	0	0.658736	3.667123	1.750195
41	1	0	1.156165	3.955734	2.673943
42	6	0	-0.246099	4.544389	1.160109
43	1	0	-0.452979	5.508014	1.618076
44	6	0	-0.872460	4.167463	-0.020046
45	1	0	-1.580093	4.835168	-0.505696
46	6	0	-5.917946	-0.655857	-0.776194
47	1	0	-6.280565	-1.648219	-1.062435
48	1	0	-6.455689	-0.344702	0.123647
49	1	0	-6.197359	0.033155	-1.581767
50	1	0	4.802717	1.318336	-2.758051
51	1	0	-0.347228	-4.204882	2.705186
52	9	0	-0.122768	0.729795	-2.075533
53	6	0	1.952048	1.545139	1.898368
54	1	0	2.246194	1.983867	2.857008
55	1	0	1.560931	0.541627	2.089679
56	1	0	2.853271	1.409169	1.292768
57	1	0	-1.075361	2.638665	-1.505831

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=THF,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.59191858 a.u.

Excited State 1: Singlet-A 3.2078 eV 386.51 nm f=0.2090
<S**2>=0.000
108 ->109 0.69409

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=THF, NonEquilibrium=Read)

SCF Done: E(RCAM-B3LYP) = -1261.70870311 a.u.

Results

Absorb Energy =	0.138 a.u.	3.751 eV	330.574 nm
Emission Energy =	0.117 a.u.	3.178 eV	390.149 nm
Stokes Shift =	0.021 a.u.	0.573 eV	59.575 nm

Acetonitrile

Step1

Method: cam-b3lyp/6-31G(d)
Solvent : Acetonitrile
SCF Done: E(RCAM-B3LYP) = -1261.63731826 a.u.
Lowest frequency = 16.9299

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.194278	-0.586739	-0.070440
2	5	0	0.552292	0.617404	-0.722229

3	6	0	2.126601	0.285428	-0.812562
4	6	0	2.957756	1.184872	-1.492353
5	1	0	2.518226	2.103359	-1.875874
6	6	0	4.310899	0.950171	-1.687918
7	6	0	4.864964	-0.233473	-1.203867
8	1	0	5.918786	-0.451040	-1.355586
9	6	0	4.065137	-1.143660	-0.531813
10	1	0	4.521822	-2.065920	-0.189978
11	6	0	2.696662	-0.897603	-0.313156
12	6	0	1.843455	-1.866131	0.414731
13	6	0	2.400926	-2.978390	1.055960
14	1	0	3.479281	-3.090997	1.064933
15	6	0	-0.331654	-2.718132	1.081203
16	1	0	-1.410575	-2.625470	1.098766
17	6	0	1.642935	-3.952043	1.689256
18	1	0	2.123508	-4.796791	2.172412
19	6	0	0.258436	-3.816138	1.681502
20	6	0	0.425748	-1.697681	0.457120
21	6	0	-0.523663	3.009787	-0.682964
22	6	0	0.254338	2.065302	-0.002471
23	6	0	0.769624	2.457620	1.254168
24	6	0	-2.219724	-1.169112	-1.330446
25	6	0	-1.384988	-1.830683	-2.395448
26	1	0	-0.810122	-2.665414	-1.979322
27	1	0	-2.018637	-2.223193	-3.195970
28	1	0	-0.671959	-1.119617	-2.812615
29	6	0	-2.441639	-0.115366	0.844777
30	6	0	-1.624599	-0.613254	-0.182420
31	6	0	-1.861784	0.358175	2.151264
32	1	0	-1.326288	1.302589	2.036758
33	1	0	-2.653797	0.499469	2.892362
34	1	0	-1.147835	-0.369053	2.549381
35	6	0	-3.606892	-1.144026	-1.460667
36	1	0	-4.056324	-1.571426	-2.354652
37	6	0	-4.431665	-0.600365	-0.478780
38	6	0	-3.827361	-0.110363	0.673831
39	1	0	-4.450770	0.278584	1.476155
40	6	0	0.490932	3.726942	1.765952
41	1	0	0.894883	4.004851	2.737610
42	6	0	-0.291738	4.640387	1.065315
43	1	0	-0.495773	5.621773	1.485324
44	6	0	-0.804424	4.275633	-0.171926
45	1	0	-1.418808	4.971049	-0.738884
46	6	0	-5.927132	-0.548676	-0.659534
47	1	0	-6.291415	-1.409276	-1.228620
48	1	0	-6.445583	-0.533029	0.303520
49	1	0	-6.230705	0.351824	-1.206735
50	1	0	4.928759	1.671543	-2.216273
51	1	0	-0.371914	-4.564188	2.155446
52	9	0	0.063603	0.757363	-2.086004
53	6	0	1.631420	1.529765	2.078381
54	1	0	1.722050	1.890196	3.108196
55	1	0	1.221108	0.517428	2.103299
56	1	0	2.640761	1.448435	1.662027
57	1	0	-0.918050	2.734277	-1.656227

Step2

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=3) SCRF(Solvent=acetonitrile)

Excited State 1: Singlet-A 3.7662 eV 329.21 nm f=0.2463
<S**2>=0.000
108 ->109 0.68773

Step3

Method: cam-b3lyp/6-31+G(d,p)
SCRF(Solvent=acetonitrile,NonEquilibrium=Save)
SCF Done: E(RCAM-B3LYP) = -1261.72782459 a.u.

Step4

Method: CAM-B3LYP/6-31+G(d,p) TD(NStates=1,Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Read)

After PCM corrections, the energy is -1261.58894786 a.u.

Excited State 1: Singlet-A 3.7649 eV 329.31 nm f=0.1878
<S**2>=0.000
108 ->109 0.68721

Step5

Method: cam-b3lyp/6-31G(d) opt freq(savenormalmodes) TD(NStates=1,Root=1)

Total Energy, E(TD-HF/TD-DFT) = -1261.50681541 a.u.
Lowest frequency = 20.4204

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.208043	-0.580808	-0.059558
2	5	0	0.536258	0.601927	-0.804577
3	6	0	2.074248	0.230954	-1.004786
4	6	0	2.863539	1.012685	-1.831616
5	1	0	2.404019	1.865338	-2.330024
6	6	0	4.224131	0.748991	-2.052181
7	6	0	4.804593	-0.338809	-1.387561
8	1	0	5.860608	-0.558919	-1.531780
9	6	0	4.058953	-1.143290	-0.551911
10	1	0	4.551702	-1.977810	-0.066435
11	6	0	2.655629	-0.900202	-0.339645
12	6	0	1.871089	-1.731424	0.503760
13	6	0	2.435995	-2.821614	1.248770
14	1	0	3.507454	-2.971742	1.229423
15	6	0	-0.336917	-2.494221	1.393355
16	1	0	-1.408208	-2.354900	1.461354
17	6	0	1.666800	-3.688892	1.997587
18	1	0	2.155328	-4.496274	2.537657
19	6	0	0.268240	-3.547781	2.076576
20	6	0	0.410607	-1.580607	0.619691
21	6	0	-0.599576	2.925010	-0.589307
22	6	0	0.297508	2.020609	-0.005776
23	6	0	0.917480	2.422311	1.198877
24	6	0	-2.190940	-1.314644	-1.273767
25	6	0	-1.312844	-2.057749	-2.245536
26	1	0	-0.696401	-2.802540	-1.731691
27	1	0	-1.918831	-2.576817	-2.992684
28	1	0	-0.638512	-1.365729	-2.753474

29	6	0	-2.471126	0.011602	0.750985
30	6	0	-1.641018	-0.620474	-0.180670
31	6	0	-1.943225	0.693372	1.986933
32	1	0	-1.815630	1.767395	1.825381
33	1	0	-2.644021	0.559120	2.816548
34	1	0	-0.975026	0.291653	2.288459
35	6	0	-3.571018	-1.318329	-1.438802
36	1	0	-3.994388	-1.852533	-2.286341
37	6	0	-4.423808	-0.664144	-0.548472
38	6	0	-3.853760	-0.021686	0.541613
39	1	0	-4.498961	0.466180	1.268829
40	6	0	0.618757	3.667118	1.756030
41	1	0	1.104993	3.956254	2.685428
42	6	0	-0.282224	4.542704	1.157065
43	1	0	-0.496416	5.505175	1.613722
44	6	0	-0.895452	4.165546	-0.029903
45	1	0	-1.599847	4.831862	-0.521839
46	6	0	-5.914512	-0.661936	-0.768481
47	1	0	-6.276998	-1.652614	-1.060110
48	1	0	-6.450015	-0.355994	0.134293
49	1	0	-6.195501	0.031497	-1.569577
50	1	0	4.813899	1.372844	-2.717829
51	1	0	-0.328639	-4.235409	2.665909
52	9	0	-0.110596	0.727844	-2.080348
53	6	0	1.911798	1.545752	1.918399
54	1	0	2.202960	1.989624	2.875347
55	1	0	1.512069	0.546622	2.115534
56	1	0	2.815636	1.398866	1.319401
57	1	0	-1.078592	2.639162	-1.519942

Step6

Method: cam-b3lyp/6-31+G(d,p) TD(NStates=1, Root=1)
SCRF(Solvent=acetonitrile,ExternalIteration,NonEquilibrium=Save)
After PCM corrections, the energy is -1261.60131641 a.u.

Excited State 1: Singlet-A 3.1974 eV 387.77 nm f=0.2126
<S**2>=0.000
108 ->109 0.69425

Step7

Method: cam-b3lyp/6-31+G(d,p) SCRF(Solvent=acetonitrile,
NonEquilibrium=Read)

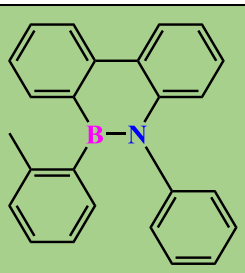
SCF Done: E(RCAM-B3LYP) = -1261.71722372 a.u.

Results

Absorb Energy =	0.139 a.u.	3.779 eV	328.085 nm
Emission Energy =	0.116 a.u.	3.154 eV	393.102 nm
Stokes Shift =	0.023 a.u.	0.625 eV	65.017 nm

5.1.10 Isosurface maps of molecular orbitals of interest

For the visualization of the molecular orbitals of interest, the isovalue of the plots was set to |0.02|.

 1	**THF**
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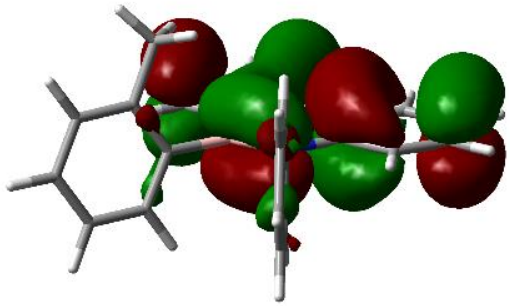	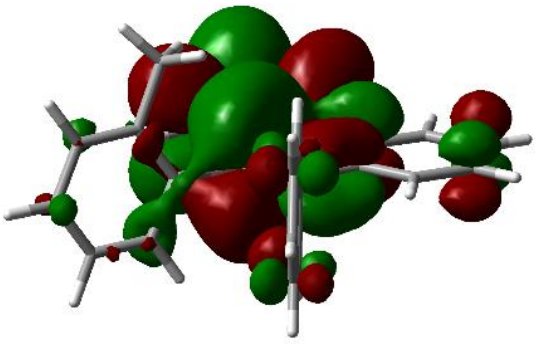
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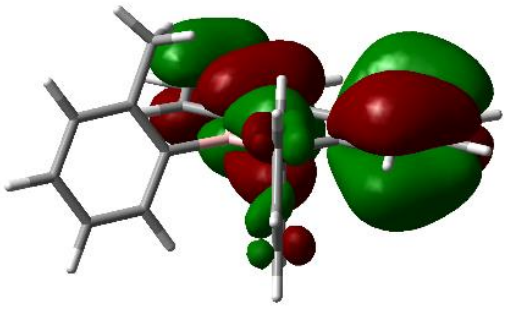	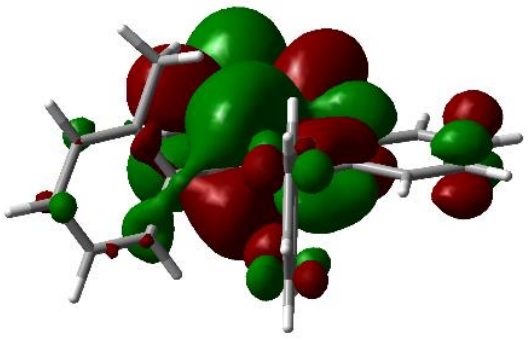
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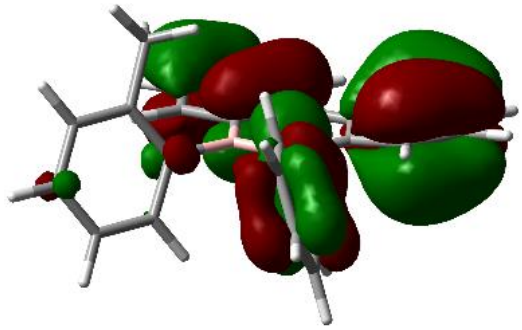	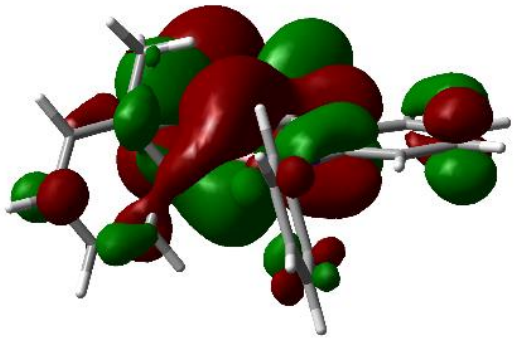
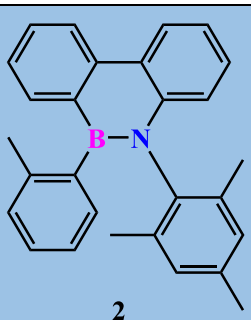 2	**THF**
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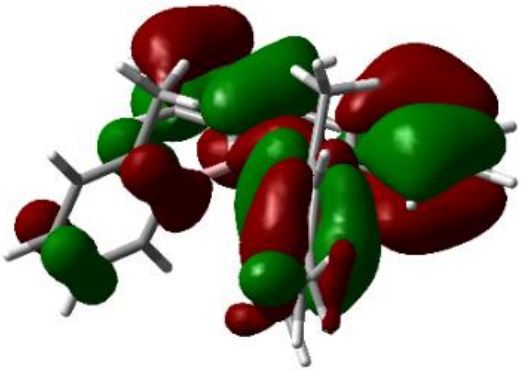	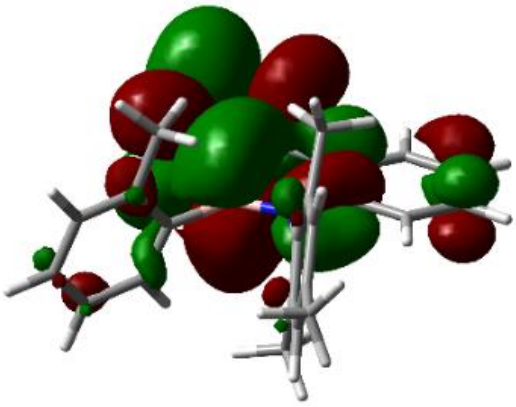
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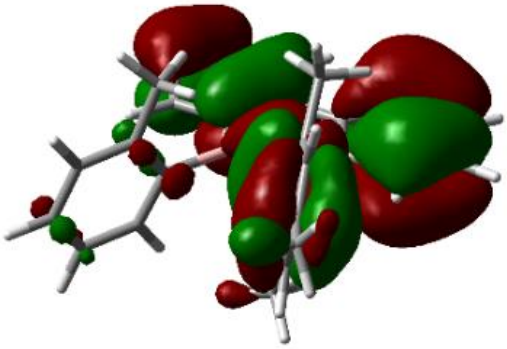	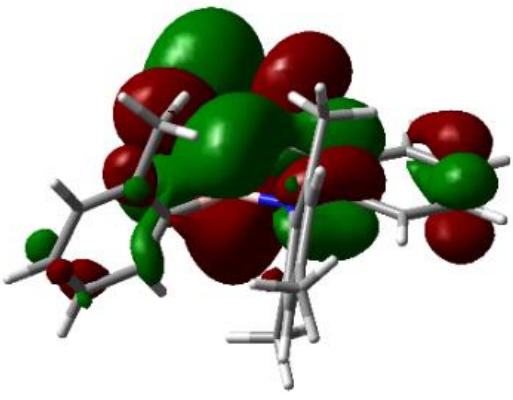

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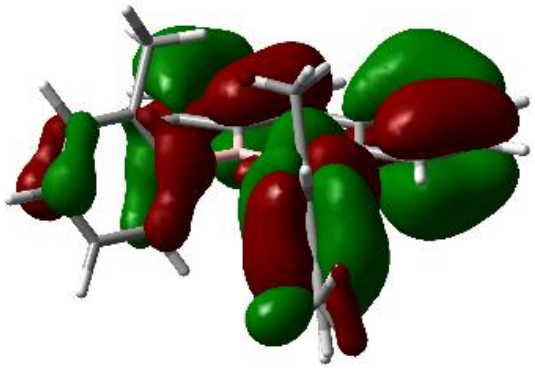	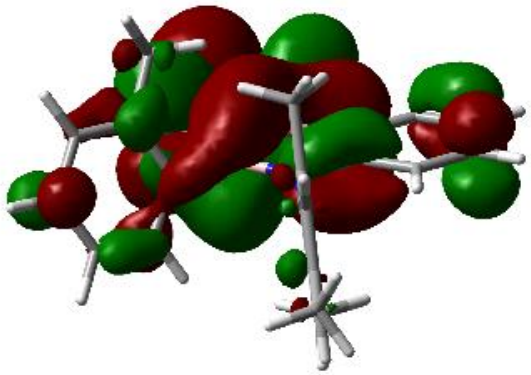
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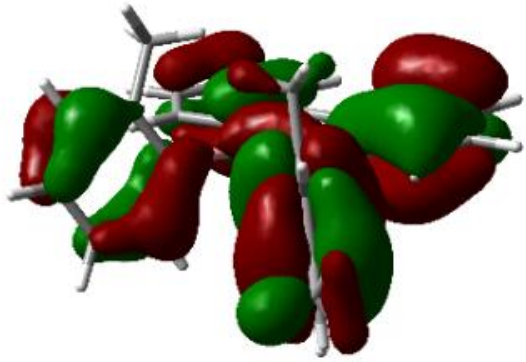	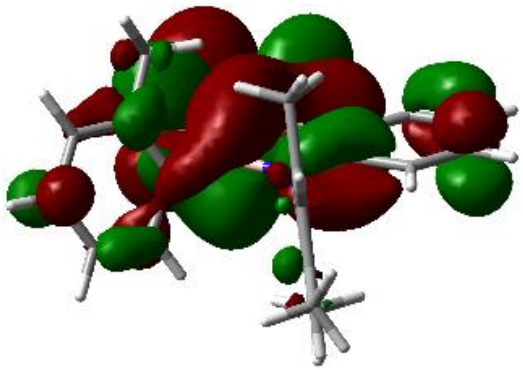
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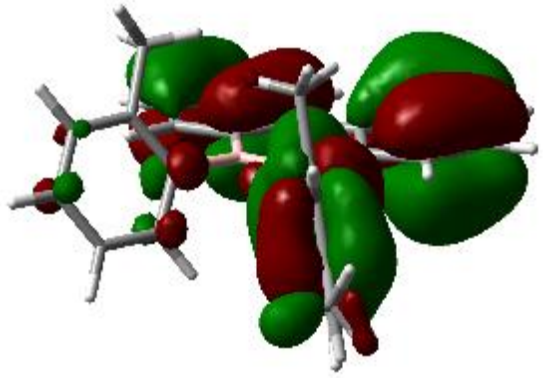
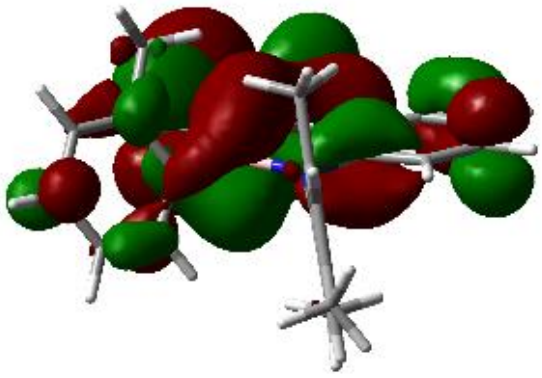
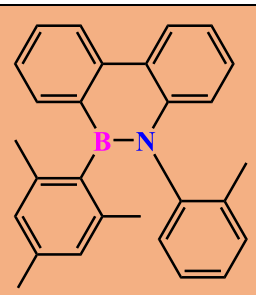
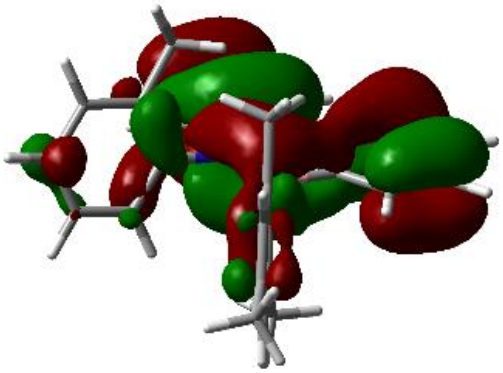
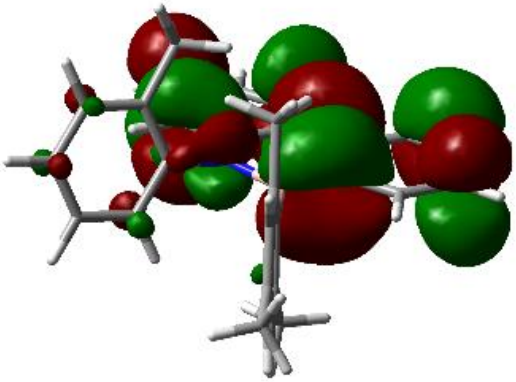
	

 3	THF
GS1_STEP 4_HOMO	GS1_STEP 4_LUMO
	
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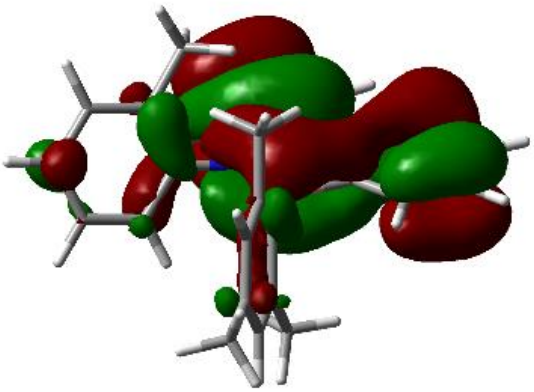
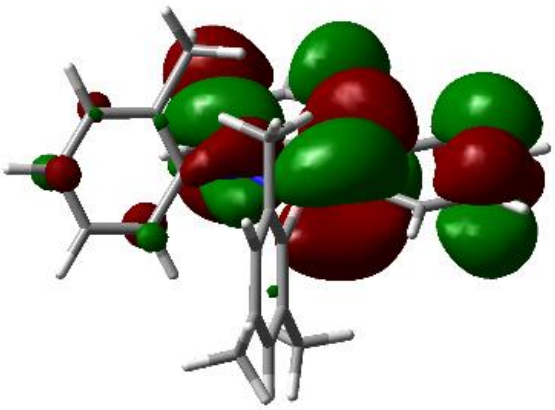
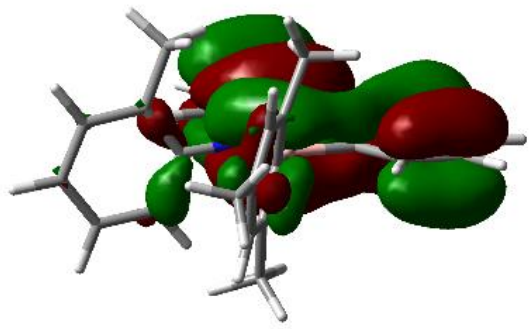
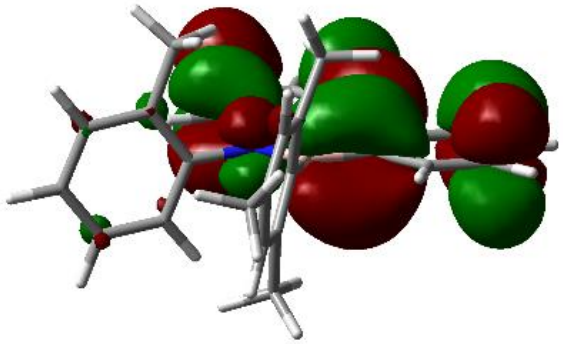
	
GS2_STEP 4_HOMO	GS2_STEP 4_LUMO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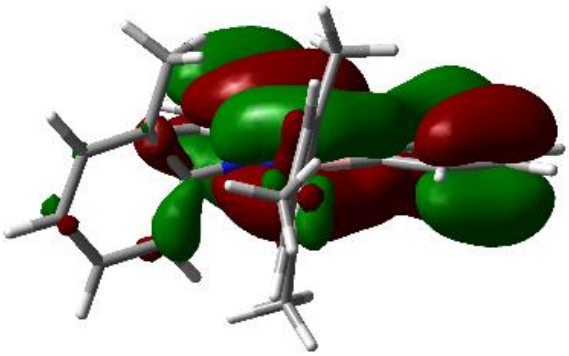	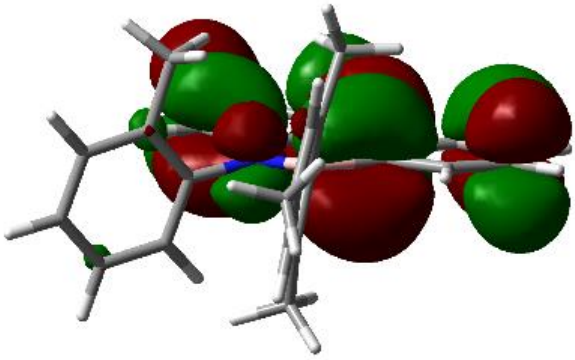
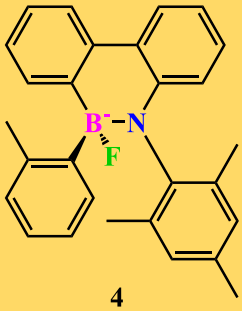 **4**	**THF**
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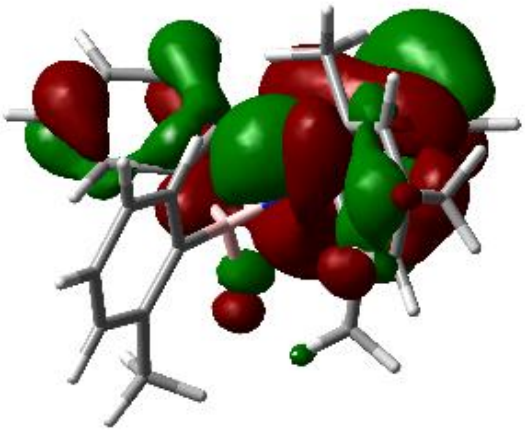	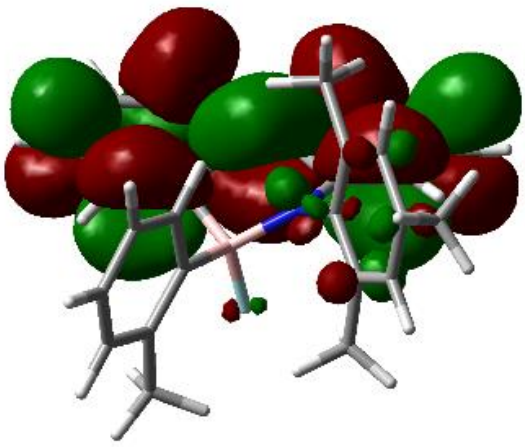

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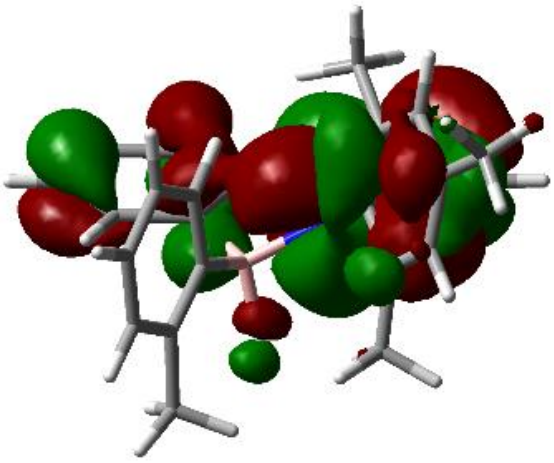	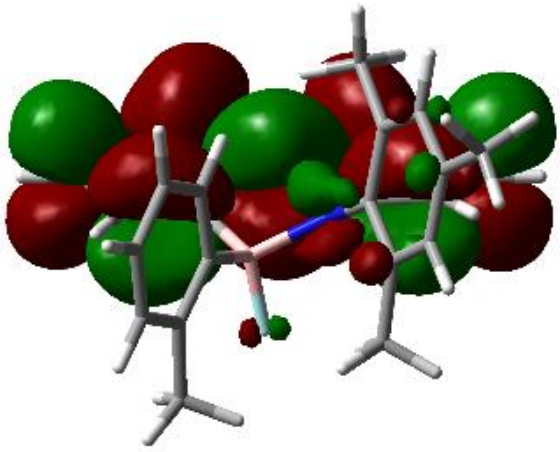
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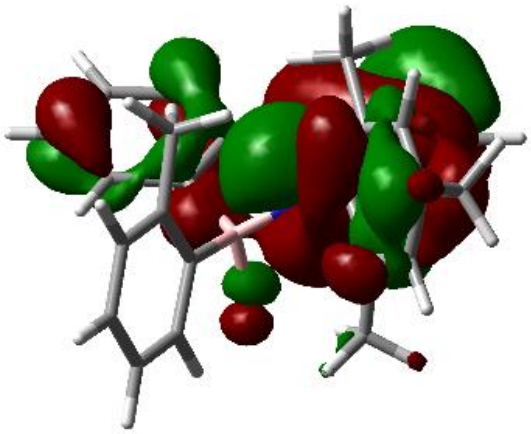	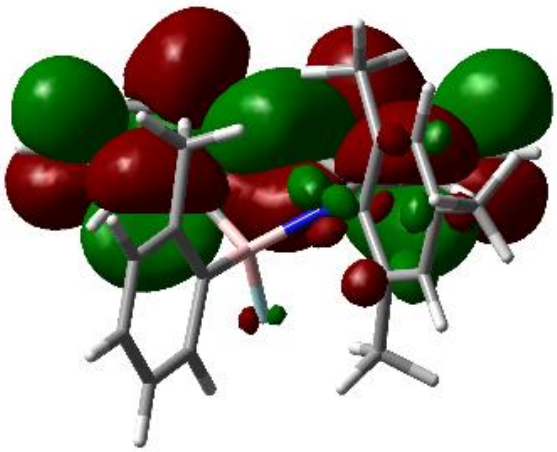
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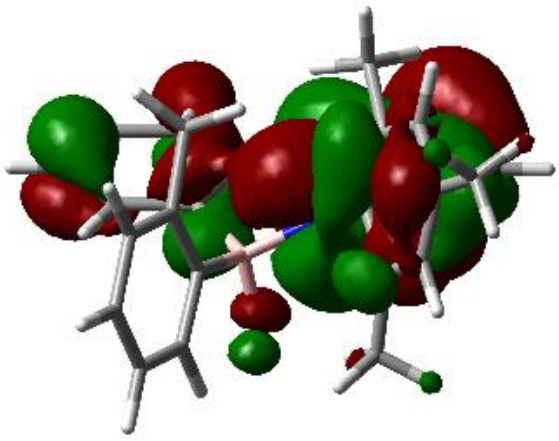	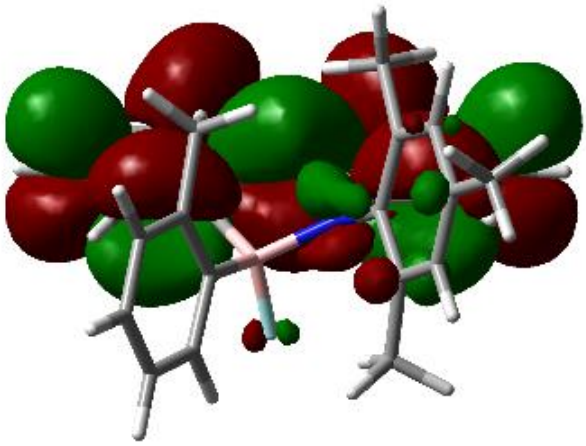
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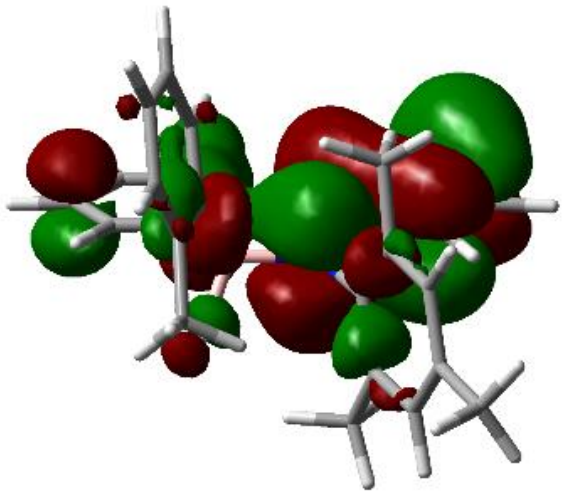	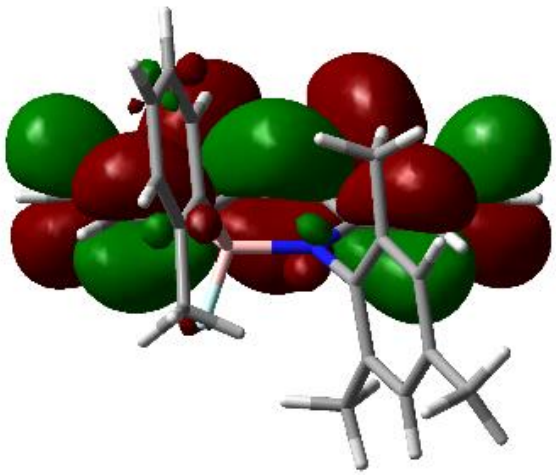
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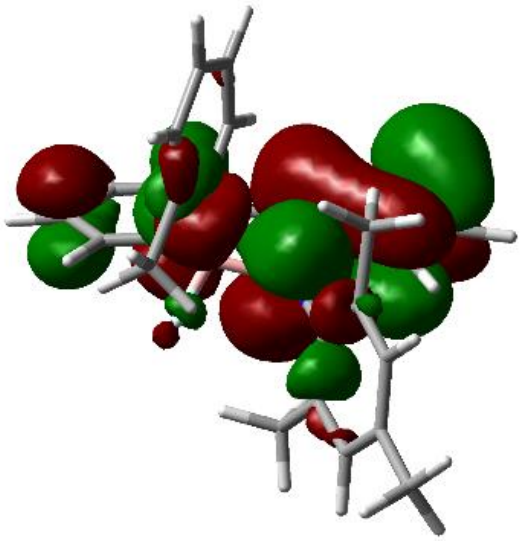	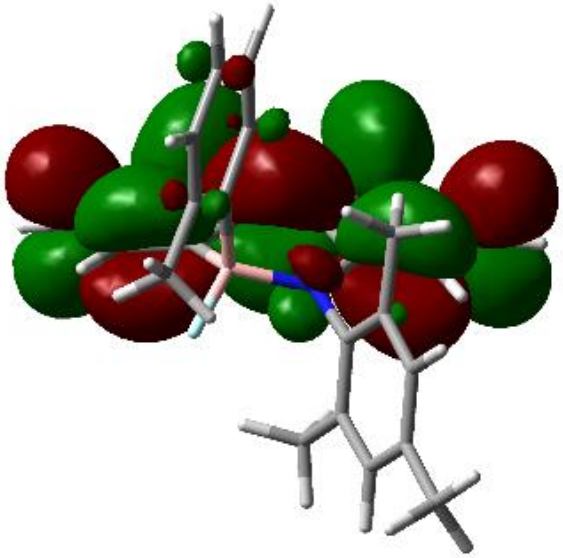
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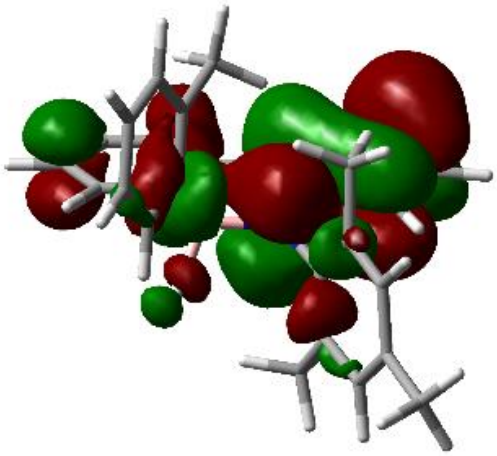
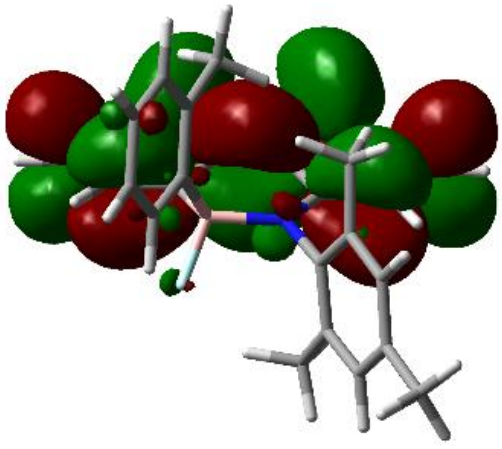
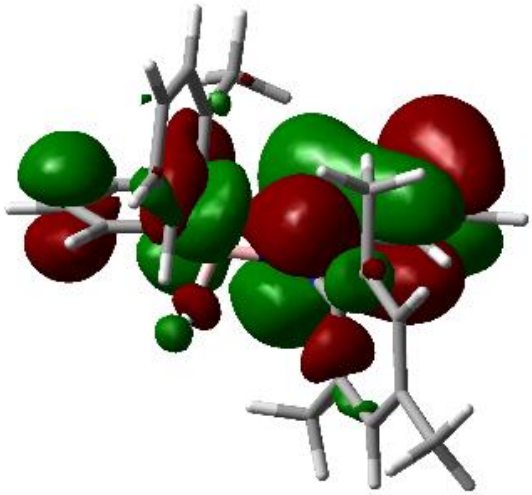
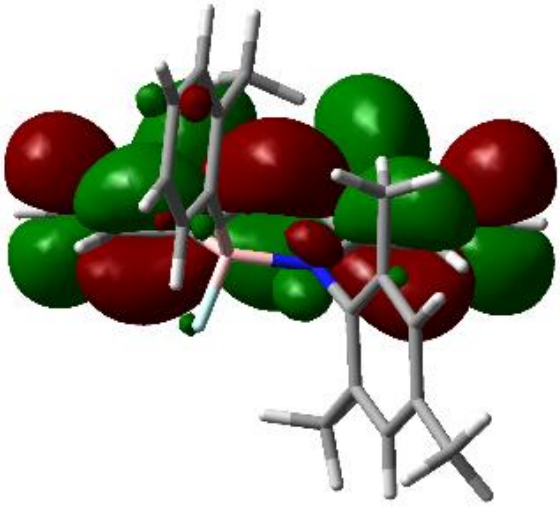
	

GS2-180-R_STEP 6_HOMO	GS2-180-R_STEP 6_LUMO
	

5.2 Materials and instrumentation

All manipulations are performed in an inert atmosphere of a constant N_2 flux, using a standard Schlenk line since no glovebox equipment is available. All the glassware used are stored in an oven at ~70°C overnight, or at least for four hours prior to being used, so as to be dry.

The commercially available reagents used are the following: *n*-butyl lithium (1.6 M in hexane), dibutyltin dichloride, 2,4,6-trimethylaniline, 2-isopropylaniline, sodium nitrite, sodium azide, acetic acid (glacial), sodium sulfate (anhydrous), 1-bromo-2-ethylbenzene, magnesium, iodine, boron trichloride, methanol, isopropanol, *n*-hexane, petroleum ether, dichloromethane, diethyl ether, ethyl acetate and toluene. Dried solvents are obtained by distillation: toluene is distilled on calcium hydride and is stored anhydrous on molecular sieve beads, while diethyl ether is distilled with sodium/benzophenone. Deuterated solvents for NMR spectra are also commercially available.

The starting reagent 2,2'-dibromo-1,1'-biphenyl had already been synthesized by another member of the lab, according to a previous work[27].

For chromatography, the following stationary phases were used:

- Column chromatography: silica gel (Merck, grade 9385, 60 Å, 230-400 mesh)

- TLC plates: silica gel 60 F_{254} aluminum plates

For HPLC, a semi-preparative HPLC Waters^{TM} 600 with a 254 nm lamp was used. The column employed for reversed-phase HPLC was the following:

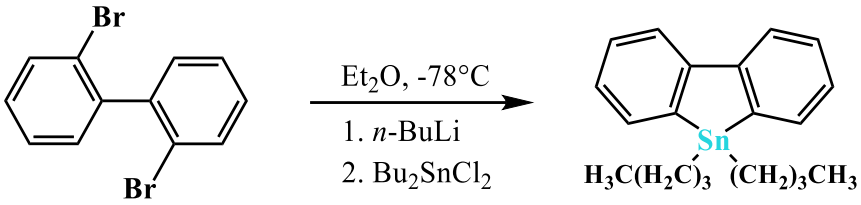
- Synergi RP1 250 x 21,20, with a flow rate of 20 mL/min and an azeotropic mixture of ACN:H_2O (90:10) as eluent.

^{1}H-NMR and ^{11}B-NMR spectra are recorded at +25°C on a Varian Mercury Plus 400 MHz and a Varian Unity Inova 600 MHz spectrometer.

Mass spectra are obtained with a Waters Micromass ZQ 4000 spectrometer in Electrospray Ionisation (ESI).

5.3 Experimental procedures

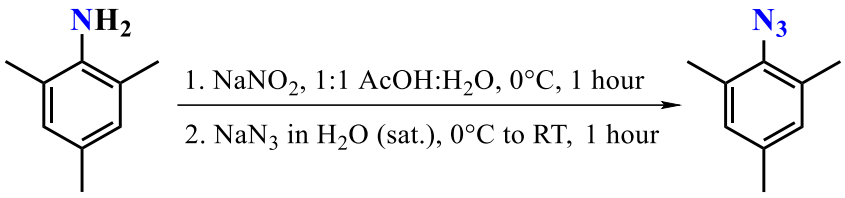
5.3.1 Formation of the 9-stannafluorene derivative



5

5,5-dibutyl-5*H*-dibenzo[*b,d*]stannole (5). In a three-neck flask equipped with a magnetic stirrer and under N_2 atmosphere, a solution of 2,2'-dibromo-1,1'-biphenyl (2 g, 6.41 mmol) in dry Et_2O (60 mL) is prepared. Then, *n*-BuLi (1.6 M in hexane, 9 mL, 14.4 mmol) is added via syringe dropwise, while the temperature is being kept below -78°C. After the addition of *n*-BuLi, the reaction solution is let to cool down to room temperature and is stirred overnight. A solution of Bu_2SnCl_2 (1.95 g, 6.42 mmol) in Et_2O (5 mL) is added dropwise to the above solution via syringe, at -78°C. The solution is let to cool down and is stirred overnight. The reaction mixture is filtered and the solvent in the filtrate is removed *in vacuo*. The crude is purified by column chromatography (*n*-hexane as eluent), affording the product **5** (0.631 g, 25.6%) in the form of a white crystalline solid; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.95 (m, 2H), 7.62 (ddd, 2H), 7.39 (dt, 2H), 7.27 (dt, 2H), 0.87 (t).

5.3.2 Preparation of the azide



8

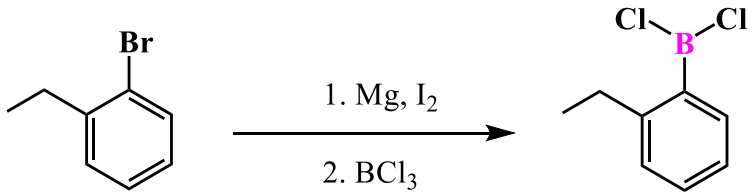
2-azido-1,3,5-trimethylbenzene (8).[25] In a cooled solution (0°C) of 2,4,6-trimethylaniline (1.62 g, 12.0 mmol) in 20 mL of AcOH and H_2O (50:50, *v/v*), a saturated solution of $NaNO_2$ (1.29 g, 18.7 mmol) in H_2O is added dropwise. The mixture is allowed to reach room temperature and, in the

meantime, it turns from orange to colorless and then to yellowish. After 1 hour of stirring, a saturated solution of NaN_3 (2.79 g, 22.0 mmol) in H_2O is added dropwise at 0°C and the bubbling reaction mixture is allowed to cool down to room temperature and is let stirring for 1 hour. Afterwards, the reaction mixture is diluted with 30 mL of H_2O and 30 mL of Et_2O and saturated, liquid $NaHCO_3$ is added until the pH of the aqueous phase reaches 7. The phases are separated and the resulting aqueous phase is extracted with an additional 2 x 30 mL of Et_2O. The combined organic phases are washed with 1 x 20 mL of distilled H_2O and 1 x 20 mL of brine. The resulting organic phase is dried over Na_2SO_4 and the heterogeneous mixture is filtered. The filtrate is concentrated *in vacuo* and the desired mesitylazide **8** is obtained as an orange oil (1.74 g, 90%); ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 6.83 (m, 2H), 2.32 (s, 6H), 2.25 (s, 3H).

5.3.3 Towards the synthesis of the BNP product

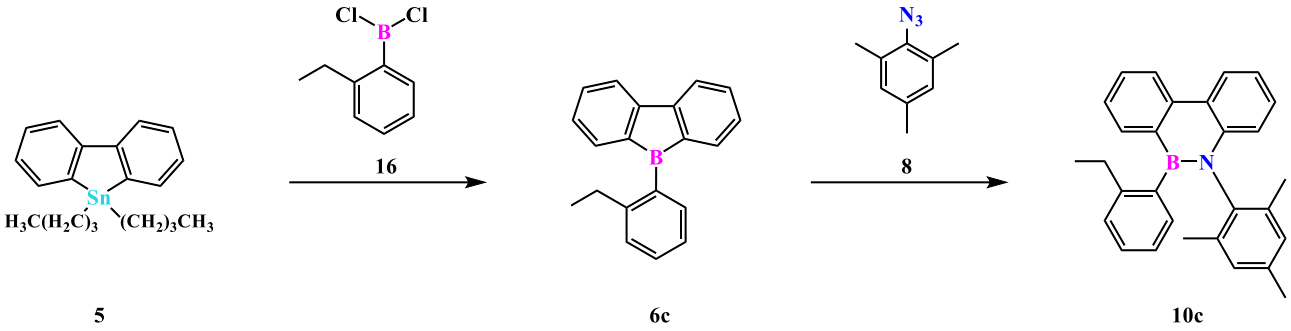
Activation of Mg:

Solid Mg is added in a flask equipped with a magnetic stirrer for solids. It is washed four times with a solution of HCl (0.1 M), twice with a solution of HCl (1 M) and then it is washed with distilled water, isopropanol and Et_2O successively. It is dried *in vacuo* and finally, it is placed in the oven at 67-70°C, in order to stay dry and avoid been oxidized, until needed.



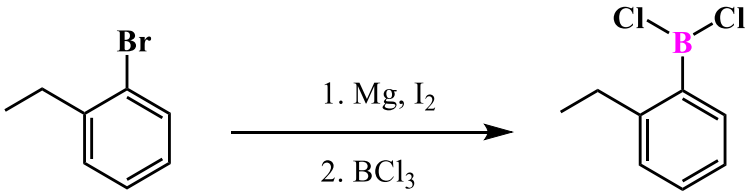
16

Dichloro(2-ethylphenyl)borane (16). In a 10 mL oven-dried two-neck flask equipped with a magnetic stirrer and under N_2 flow, 1-bromo-2-ethylbenzene (0.07 mL, 92.5 mg, 0.5 mmol) is added in activated magnesium (37 mg, 1.5 mmol) and a tip of iodine and then, dry Et_2O (3 mL) is added. The reaction mixture is heated to reflux and is let stirring for 2 hours. Afterwards, it is let to cool down to room temperature. Subsequently, Et_2O is removed *in vacuo* and dry toluene (5 mL) is added (0.1 M). In a 25 mL two-neck flask equipped with a magnetic stirrer, boron trichloride (BCl_3) in hexanes (1 M, 0.5 mL, 0.5 mmol) is brought to -78°C in an acetone bath and the Grignard reagent formed in the previous flask is transferred with a syringe, under N_2 flow. The resulting solution is left to stir overnight at room temperature.



5 6c 10c

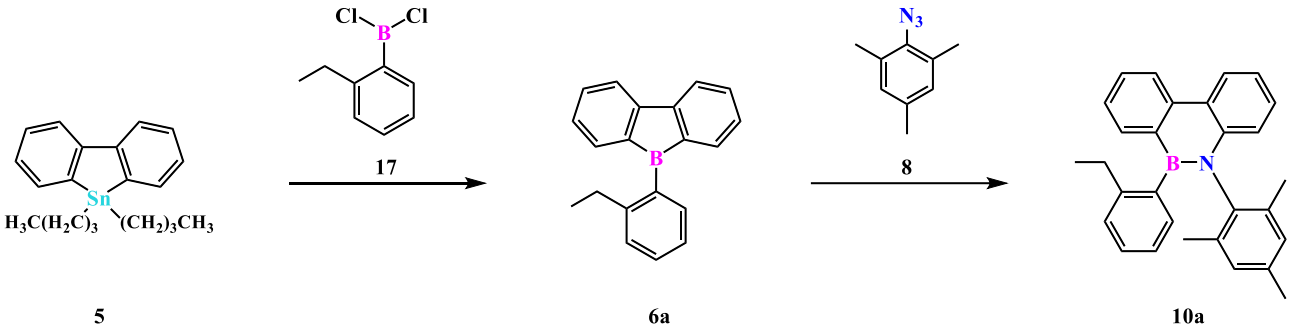
6-(2-ethylphenyl)-5-mesityl-5,6-dihydrodibenzo[*c*,*e*][1,2]azaborinine (10c).[1] In an oven-dried 25 mL two-neck flask with a magnetic stirrer and under N_2 flow, 9-stannafluorene **5** (192.6 mg, 0.5 mmol) is dissolved in dry toluene (5 mL) and the red/pink solution of the previously formed **16** (theoretically 93.4 mg, 0.5 mmol) is added dropwise at -78°C via cannula (temperature raised up to -20°C as the addition was fast). The reaction solution is slowly warmed to room temperature and is let stirring for 8 hours. The solution from red/pink turns into orange and subsequently to yellow in the first 15 minutes of stirring, while after 8 hours it becomes colorless. Subsequently, the azide **8** (0.1 g, 0.6 mmol) in dry toluene (2 mL) is added dropwise at 40°C and the solution stirs overnight at this temperature. The solution is washed with Et_2O and a white solid is formed. The solvent system is removed *in vacuo*, the resulting heterogeneous mixture is washed with AcOEt and the white solid (inorganic, insoluble in ethyl acetate) is filtered with celite. The solvent is once more removed *in vacuo* and the product is purified with column chromatography in isocratic elution mode with petroleum ether and in the end EtOAc is added, in order to collect the last, polar fraction. Three fractions are obtained. From these three, the first is characterized by NMR and is found to be $MesN_3$, while the second is checked by NMR and separated in 6 fractions (5.8 min, 7 min, 8.1-9.7 min, 9.8 min, 11.3 min, 12.3 min) with HPLC (C18 column, azeotropic eluent ACN:H_2O 90:10, flow rate: 20 mL/min).



17

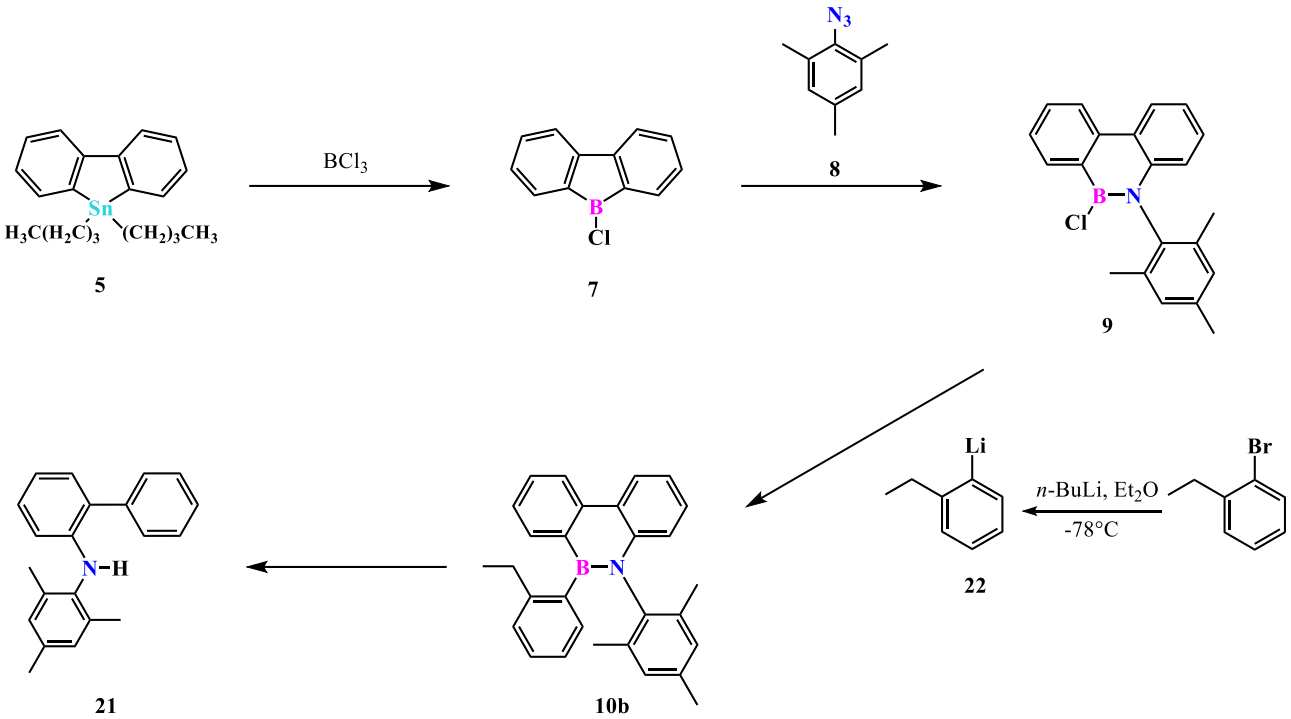
Dichloro(2-ethylphenyl)borane (17). In a 10 mL oven-dried two-neck flask equipped with a magnetic stirrer and under N_2 flow, 1-bromo-2-ethylbenzene (0.07 mL, 92.5 mg, 0.5 mmol) is added in activated magnesium (73 mg, 3 mmol) and iodine and then, dry Et_2O (3 mL) is added. The reaction mixture is heated to reflux and is let stirring for 2 hours. Afterwards, it is let to cool down to room temperature. Subsequently, Et_2O is removed *in vacuo* and dry toluene (5 mL) is added (0.1 M

concentration). In a 50 mL three-neck flask equipped with a magnetic stirrer, boron trichloride (BCl_3) in hexanes (1 M, 0.5 mL, 0.5 mmol) in dry toluene (5 mL) is brought to -78°C in an acetone bath and the Grignard reagent formed in the previous flask is transferred with a syringe, under N_2 flow. The resulting solution (orange and the next day red) is left to stir overnight at room temperature.



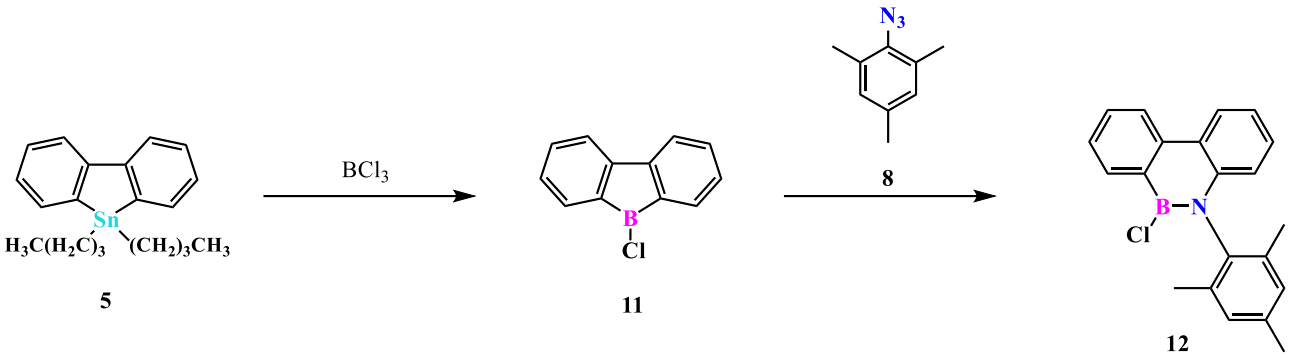
5 6a 10a

6-(2-ethylphenyl)-5-mesityl-5,6-dihydrodibenzo[*c,e*][1,2]azaborinine (10a).[1] A solution of 9-stannafluorene **5** (192.6 mg, 0.5 mmol) in dry toluene (5 mL) is added dropwise via syringe in the mixture of the previously formed **17** (theoretically 93.4 mg, 0.5 mmol) at -78°C, under N_2 atmosphere and the reaction solution is slowly warmed to room temperature and is let to stir overnight. The solution from red turns into orange, subsequently to yellow and at the end it becomes colorless. Then, azide **8** (100 mg, 0.62 mmol) in dry toluene (2 mL) is added dropwise at -78°C and after the addition is over, the solution (yellow) is allowed to reach room temperature and is then heated to reflux and is let stirring overnight. The resulting heterogeneous mixture is filtered with celite and the solvent is removed *in vacuo*. Column chromatography of the crude is performed with petroleum ether/ethyl acetate 50:1.



6-(2-ethylphenyl)-5-mesityl-5,6-dihydrodibenzo[*c*,*e*][1,2]azaborinine (10b).[7] In an oven-dried 10 mL two-neck flask equipped with a magnetic stirrer, a solution of 9-stannafluorene **5** (192.6 mg, 0.5 mmol) in dry toluene (3 mL) is cooled to 0˚C upon which BCl_3 in hexanes (1 M, 0.5 mL, 0.5 mmol) is added rather fast. The reaction solution (yellow) is then stirred for 22 hours at room temperature. The volatiles are removed *in vacuo*, while Bu_2SnCl_2 by-product is removed by sublimation (50-55˚C, 0 mbar) to give a yellow solid residue. Then, the azide **8** (102 mg, 0.63 mmol) in toluene (2 mL) is added dropwise under N_2 atmosphere to a cooled (0°C) solution of the previously obtained yellow residue in dry toluene (3 mL). The solution is allowed to reach room temperature and is then heated to reflux and is let stirring overnight, after which the solution becomes dark brown/black.

In an oven-dried 25 mL three-neck flask, 1-bromo-2-ethylbenzene (0.22 mL, 296 mg, 1.6 mmol) is dissolved in dry Et_2O (8 mL) and is cooled at -78°C, upon which *n*-BuLi (1 mL) is added dropwise, under N_2 flow to afford the lithiated derivative **22** after 1 hour of stirring at room temperature. From this solution, 2.9 mL (theoretically 0.5 mmol of the product **22**) are transferred via syringe dropwise at -78°C in the solution of **9** (theoretically 0.5 mmol). The reaction solution is stirred at this temperature for 1 hour after which the cold acetone bath is removed and is then let to stir at room temperature for another 3 hours. The resulting heterogeneous mixture is filtered with celite and the volatiles are removed *in vacuo*. Column chromatography is performed with *n*-hexane and is finished with increasing amounts of DCM to afford **21** (0.0178 g, 12.4%) as an orange/red crystalline solid instead of the expected product **10b**.



5 11 12

6-chloro-5-mesityl-5,6-dihydrodibenzo[*c,e*][1,2]azaborinine (12). In an oven-dried 50 mL two-neck flask equipped with a magnetic stirrer, a solution of 9-stannafluorene **5** (191.2 mg, 0.5 mmol) in dry toluene (3 mL) is cooled to 0˚C upon which BCl_3 in hexanes (1 M, 0.5 mL, 0.5 mmol) is added dropwise, under N_2 atmosphere. The reaction solution (yellow) is then stirred for 27 hours at room temperature. The solution is cooled at 0°C and the azide **8** (103 mg, 0.64 mmol) in toluene (2 mL) is added dropwise under N_2 atmosphere. The solution is let to reach room temperature, then is heated to reflux and is let stirring for 19 hours. The solution becomes orange, then deep red and finally brown/black. The solution is let to cool down to room temperature and the reaction is quenched with the addition of MeOH (1 mL, 1.5 hour). The volatiles are removed along with the solvent *in vacuo*.

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