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Grau de Química

Treball Final de Grau

Molecular rotors: novel luminescent organic materials. Preparation and photophysical characterization.

Rotors moleculars: nous materials orgànics luminiscents. Preparació i caracterització fotofísica.

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REPORT

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1. SUMMARY

This Final Degree Thesis has been focused on the synthesis and study of optical properties of different 9H-carbazole derivatives to, subsequently, keep working with these organic compounds in technologic applications such as haptic interfaces. To obtain the desired compounds, we have modified the 9H-Carbazole structure to introduce in it a bond which allows it to rotate on itself (this kind of compounds are called molecular rotors), providing it with more rigidity to make the product has rotative properties more sensitives to the viscosity environment and it has also been added some functional groups to allow the molecule to form hydrogen bonding with a protic solvent because our study is based on the study of how the compound changes its photochemical behaviour depending on the viscosity and nature of the environment where they are placed in.

Synthetic routes that have been followed are very known reactions and have not been a difficulty to the researching work. The chemical structure of our synthetized compounds has been characterized through different spectroscopy techniques such as ^{1}H-NMR, ^{13}C-NMR, mass spectroscopy and IR that are the most common techniques used in conventional organic chemistry.

It has been studied the possible interrelation between the solvent viscosity and the optical properties of the desired compounds as well as the interrelation between the solvent nature and these properties. To perform this study, some instrumental techniques have been used such as absorption and emission spectroscopy. Finally, we have observed that there is an interrelation between the fluorescence activity of the dyes and the viscosity of the environment they are placed in. But when the solvent is protic, that dependence gets lost and it behaves with an anomalous dependence.

Keywords: carbazole, fluorescence, molecular rotors, viscosity, hydrogen bonding.

2. RESUM

Aquest Treball Final de Grau s'ha centrat en la preparació i estudi fotoquímic de diferents compostos fluorescents derivats del 9H-Carbazole per, posteriorment, poder continuar treballant amb aquests compostos en aplicacions tecnològiques com ho son les Haptic Interfaces. Per a la síntesi dels compostos desitjats, s'ha modificat l'estructura del 9H-Carbazole proporcionant-li un enllaç mitjançant el qual pot rotar (compostos anomenats rotors moleculars), aportant-li més rigidesa per facilitar que el compost tingui unes propietats rotatives més dependents de la viscositat del medi on es trobi i també per aportar la capacitat de formar Ponts d'hidrogen amb solvents pròtics, ja que el nostre estudi es basa en estudiar com canvia el comportament fotoquímic dels compostos sintetitzats segons la viscositat i la naturalesa del medi on es troben.

Les rutes sintètiques que s'han fet servir són reaccions molt estudiades i que no han estat motiu de cap problema pel que fa a la investigació. L'estructura química dels diferents productes obtinguts ha estat caracteritzada mitjançant l'espectroscopia de RMN tant d'hidrogen com de carboni 13, espectroscopia de masses i IR que són les tècniques de caracterització d'ús més freqüent a la química orgánica convencional.

S'ha estudiat la possible relació entre la viscositat del solvent i les propietats òptiques dels compostos així com la relació entre la naturalesa del solvent i aquestes. Per realitzar aquest estudi, hem fet ús de tècniques instrumentals com l'espectroscopia d'absorció i fluorescencia. I al final de l'estudi hem pogut observar que hi ha una relació entre la fluorescència dels fluorofors i la viscositat del medi on es troben però quan el solvent és pròtic, aquesta tendència es perd i té un comportament de dependencia anòmala.

Paraules clau: Carbazol, fluorescència, rotors moleculars, viscositat, Ponts d'hidrogen.

3.INTRODUCTION

Nowadays, searching for new materials for new technological applications is one of the most increasing areas of science. The knowledge in this science field is being improved and getting wider daily. We specially care about the interest in novel organic materials that have a huge variety of potential applications in the industry. [1]

It is known that organic materials are more suitable for technological applications because of their advantages versus the inorganic ones. Organic materials have a lower cost than inorganic ones, are easier to prepare, they have compositional flexibility and the ability to fabricate complex structures. [2]

Going deeper in novel organic materials, we realize that recently, the interest in searching for new mechano-fluorescent materials has increased because of their future applications in different fields of science and technology, for instance, to create haptic interfaces.

Haptic Interfaces are systems that allow people to interact with a computer through bodily sensations and movements. Haptics means a technological interaction between the human and the computer that includes tactile feedback or other bodily sensations to perform actions or processes on a computing device. [3]

3.1. MECHANO-FLUORESCENT MATERIALS

A mechano-fluorescent material is a substance that gives a luminescent response to external and physical stimuli. For example, a compound that emits fluorescence can modulate the intensity of its optical signal when submitted to different external pressure or tensions. However, there are different variety of mechano-optical response materials. Some, for instance, change its colour just by pressure or tension application because of the induction of a change in its physical state. [4]

In our research team, it has been studied some systems that decreased their fluorescence when a tension was applied on them. Now, it would be interesting to find some way of increasing this fluorescence. Therefore, we are using molecular rotors, because their

luminescent activity can be increased by preventing them from rotating. Furthermore, in previous works, the signal was observed in the UV region and it was more difficult to detect because it is needed the use of special instruments. So, we are interested in achieving some other materials that can emit in the Visible region to make their luminescent activity easily detectable opening a variety of future applications.

In a previous work, the carbazole derivative, with ultraviolet emission around 350nm was incorporated as a side chain chromophore to a polysiloxane matrix that exhibits elastic properties and liquid crystal behaviour. The change in the fluorescent emission of the material upon stretching of the polymer was attributed to the different proximity between the dye that emits light and the LC that absorbs the light emitted by the dye.

The structure of the polymeric system is displayed below:

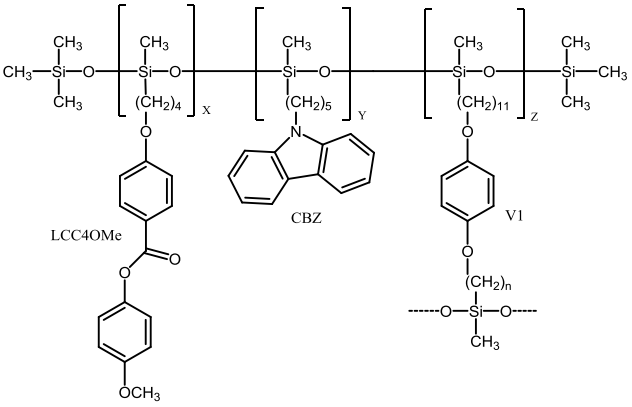


Figure 1. Chemical composition of the LSCE

3.1.1 Molecular rotors

Compounds that are named molecular rotors are ones with a special feature. They typically have a conjugated domain that can rotate freely when the compound is in low-viscosity solutions providing relaxation of the electronically excited dyes by nonradiative processes. This rotation can be controlled, restrained by increasing the viscosity of the environment. Raising the viscosity of the solution results in high fluorescent intensities. They are fluorescent molecules that can be used to know the viscosity in solutions or biological fluids. They have an uncommon fluorescent behaviour and a high capacity of giving response to external stimuli. [5]

Knowing that the more restricted is the rotation of a molecular rotor, the more luminescent intensity has, the fluorescent capacity of the compound depends directly on two main variables that can control the rotation state and that are easy to be modified by us: viscosity of solvents and nature of solvents that permit stablishing hydrogen bonding making the chemical structure more rigid and difficulties the rotation.

3.1.2. Viscosity influence on the fluorescence of the compound

Apart from the application of these kind of compounds in which we are interested in, that was mentioned above (haptic applications), there are other possible and interesting applications for rotor compounds. For instance, biomedicine. There are some diseases such as Alzheimer, Parkinson or Diabetes that are directly related to the variation of the viscosity of cellular fluid. That means that finding molecular rotors and being able to study the fluorescent behaviour they have depending on the viscosity of the environment they are, could be a huge step to the biologist researchers to study whether Alzheimer can be detected by the viscosity variation of the cellular fluid or not, and the diagnosis of certain diseases could be more accurate. [6]

Further applications are found, as for instance it has been pointed useful as replacement of current methods to measure the viscosity when the subject to measure is too bulky. For instance, in food models to determinate its quality and stability. [7] If we could standardize the viscosity value at what the compound starts emitting fluorescence, it would be easier to measure viscosity in complex samples. We could know the viscosity of an environment just placing there the fluorescent molecular rotor.

They are interesting applications although they are not the focus of our work.

Demonstrating that there is a relation between the viscosity and the fluorescence, and knowing in which way they are related, would be interesting.

3.1.3. Hydrogen bonding influence on the fluorescence of the compound

The hypothesis of the present study is: the fluorescence of a molecular rotor increases when we raise the viscosity of the environment it is solved at. And the more and the stronger hydrogen bonding the solvent/environment allows to establish, the least freedom on rotating the molecule will have.

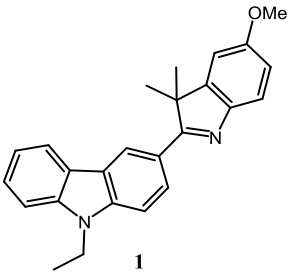
Therefore, we think that, for instance, a molecular rotor "X" is giving more fluorescent signal solved in Methanol that if it is solved in Toluene because they have the same viscosity (that is another variable that can influence the rotation and fluorescence of the molecule) but as the MeOH allows the molecule to do hydrogen bonding, it will have less facility to rotate and the fluorescence will increase.

But we need to study this deeply and prove it empirically. This topic constitutes the main objective of the present research work.

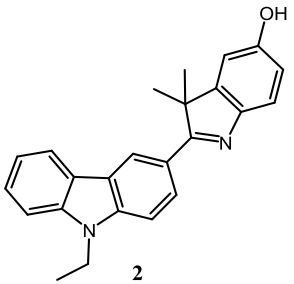
3.2. OUR FOCUSING

To achieve the synthesis of an organic material that responds to mechanical and physical stimuli by changing its luminescent behaviour and get a technological final application, a long-time of study is needed and as we cannot afford this final goal, we are starting the research by finding organic molecules, specifically molecular rotors that behave in different ways depending on the environment they are placed. To get this information, a photo physic study of the optical features of the compounds is being performed.

The compounds we are studying are:



1

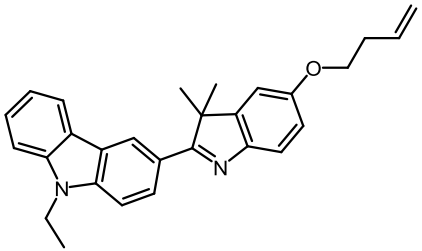


2

Figure 2. Structure of 9-ethyl-3-(5-methoxy-3,3-dimethyl-3H-indol-2-yl)-9H-carbazole (**1**) and 2-(9-ethyl-9H-carbazol-3-yl)-3,3-dimethyl-3H-indol-5-ol (**2**) respectively.

The above shown, are not suitable to be linked to any polysiloxane because an olefin is needed to undertake the addition process to bond the dye to the main chain polymer. But the photo-physical properties of these compounds should be very similar to the ones that a molecule with the olefin added (instead of the -OMe or -OH group) would have. Knowing this, we are performing our study with the two compounds above and the knowledge we get from

their behaviour in the different solvents proposed, will also be useful and totally translatable to the compound set to be bonded to the polymeric chain. **Figure 3**.



3

Figure 3. Structure of 3-(5-(but-3-en-1-yloxy)-3,3-dimethyl-3H-indol-2-yl)-9-ethyl-4a,9a-dihydro-9H-carbazolecompound **3**

To perform the study, we have chosen 9H-carbazole as platform molecule because it is easily modifiable due to its reactivity, it has a high quantum yield and it is stable thermally and photo chemically.

Depending on the results we get in the study of how hydrogen bonding can influence the luminescent behaviour of the dye, will be decided which is the better option to join the molecular rotor to the polymeric chain. As it has two possible anchor points, [figure 4] in case it exists an interrelation between the capability of forming hydrogen bounds between the dye and the solvent and the raise or loss of fluorescence signal, it will be convenient to anchor the compound by side-on because this way the group which is responsible of create these hydrogen bonds would be free to act. Whereas, if there is no interrelation between this capability and the fluorescent signal, it can be anchor by both sides indistinctly proposing a new study which consists of seeing how the point of anchor influences the dye fluorescent behaviour because of the steric hindrance.

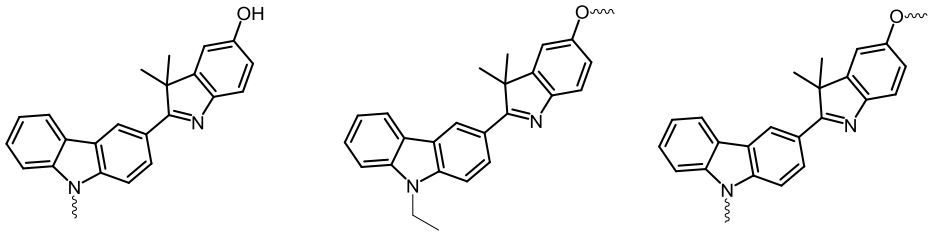


Figure 4. Anchor points of our studied compounds. Side-on (left), end-on (middle), both sides as a cross-linker (right).

In the design of these fluorescent dyes, two methyl groups have been introduced to provide the compound with some steric hindrance to give the molecule rotation dependence with viscosity.

4. OBJECTIVES

We can say that our aim is to get insights on the firsts steps, the basis of the knowledge needed, to perform the next steps to finally achieve the final goal that we have mentioned before.

The main objective in this study is to synthesize carbazole derivatives, with the property of being molecular rotors that are fluorescent compounds, blue light emitting ones, to can find ways of controlling their fluorescence. The changes in the structure made to the 9H-Carbazole are justified as follows:

On the one hand, we are increasing the Carbazole conjugation to achieve a displacement of the wavelength towards the blue region in the visible spectra. To make the signal easily detectable. On the other hand, we are providing the compound with several points of hydrogen bonding. There are two main points which can form hydrogen bonds; the nitrogen closer to the phenol group is one of them but a more effective one is the alcohol group. They can form hydrogen bounds with the solvent.

First, we are studying how different variants can influence and how the fluorescence of this kind of compounds changes and, in a second grade, we want to obtain the proper molecule structure to be bonded to a polymer to test, in a future, about how the luminescent properties change depending on the different mechanical stimuli the system receives.

To achieve those objectives, we need to perform some specific goals:

- Synthesize 3 different Carbazole derivatives.
- Chemical characterization of the molecules by ordinary techniques.
- Study their photo-physical properties.
    - The influence of environment's viscosity.
    - The influence of environment's nature. Protic, non-protic.

5. SYNTHESIS OF THE CARBAZOLE DERIVATIVES

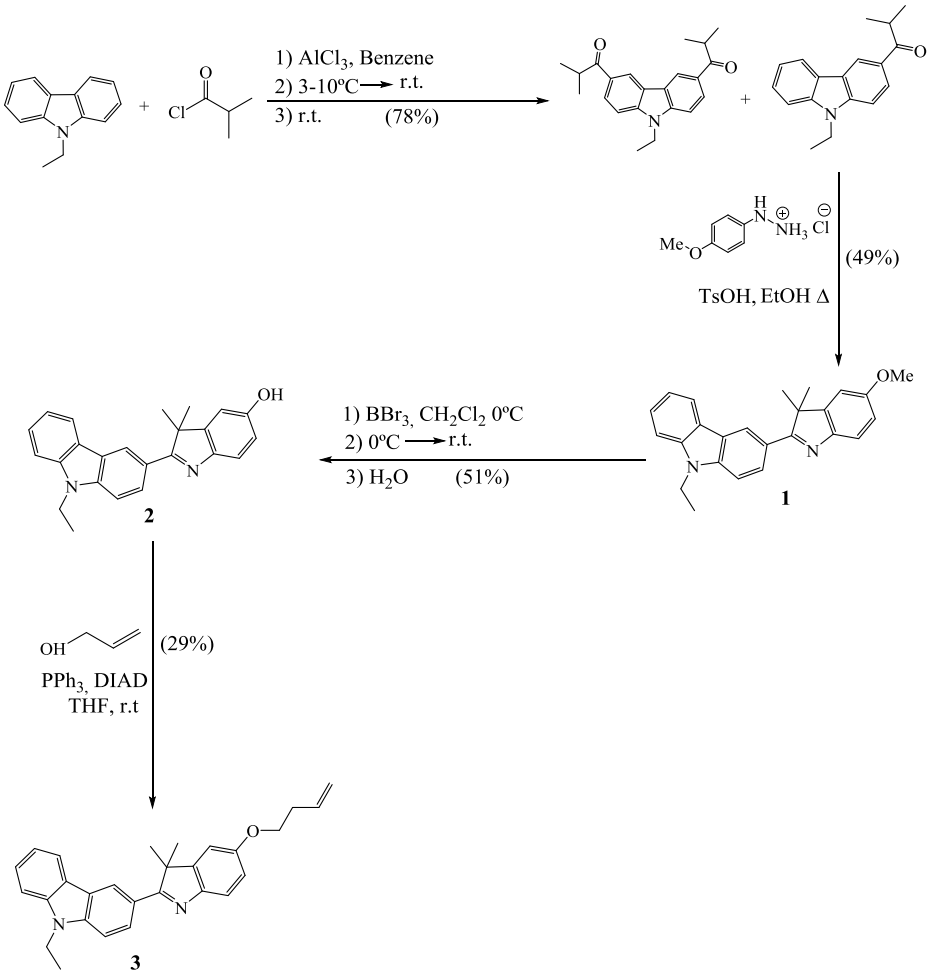


Figure 5. Synthetic procedures to obtain the carbazole derivatives **1** to **3**

The first molecule that was synthesized was 3-isobutyryl-9-ethylcarbazole. It was obtained through a Friedel Crafts acylation. It is an electrophilic aromatic substitution that allows the synthesis of mono-acylated products, when working in the right conditions, from the reaction between aromatic hydrocarbons and acyl chlorides (as it is in our case) or anhydrides in the presence of $AlCl_3$. We can see the mechanism of this reaction in **Appendix 1**.

As a final product we have the one that is of our interest, the mono-acylated one. But there is also another sub-product: the di-acylated. **Figure 6**.

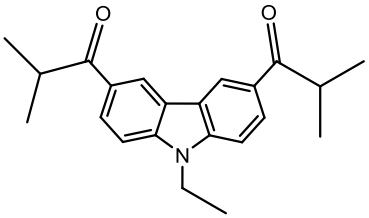


Figure 6. Chemical structure for 3,6-diisobutyryl-9-ethylcarbazole

The corresponding yield has been relatively high (77 %) what means that the selected synthetic routed is suitable for obtaining this molecule.

To obtain product **1** starting from the mono-acylated one, a Fischer Indole reaction was followed.

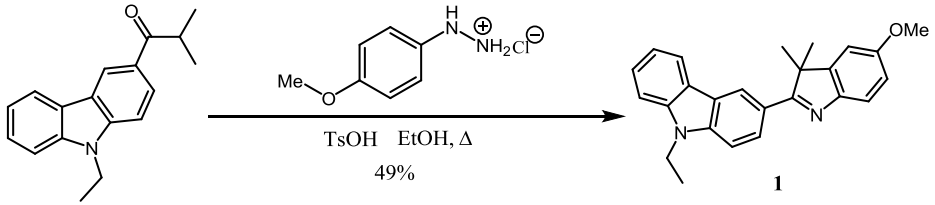


Figure 7. Synthetic procedure to obtain 9-ethyl-3-(5-methoxy-3,3-dimethyl-3H-indol-2-yl)-9H-carbazole. Derivative **1**

This reaction allows the synthesis of an indole starting from the mixture of a phenyl hydrazine (substituted) and an aldehyde in acid conditions. [8]

The substituted phenyl hydrazine and a carbonyl compound forms a phenyl hydrazone that isomerizes to the enamine. After the protonation is done, a sigmatropic [3,3] rearrangement

occurs producing the corresponding imine. The resulting imine forms a cyclic amino acetal, which under acid renders the resulting an aromatic indole, energetically favourable. [8]

We can see its reaction mechanism in **Appendix 2**.

The corresponding yield of the Fischer's step was 49%, it is a moderate yield and it is like other ones for the same reaction [4] so we consider it is correct and the mechanism followed is suitable for this obtainment.

The product obtained next was **2**. This molecule was synthetized by an O-Dealkyllation from compound **1** using boron tribromide in anhydrous dichloromethane at room temperature.

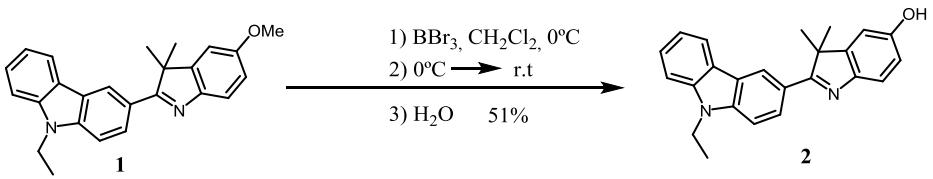


Figure 8. Synthetic procedure to obtain 2-(9-ethyl-9H-carbazol-3-yl)-3,3-dimethyl-3H-indol-5-ol. Derivative **2**

The yield of the phenol deprotection was 51%. Then, we synthetized the last product in this study: 3-(5-(but-3-en-1-yloxy)-3,3-dimethyl-3H-indol-2-yl)-9-ethyl-4a,9a-dihydro-9H-carbazole. It is compound **3**.

This compound is not being studied as **1** and **2** are. This one has been synthetized for future studies about its behaviour when this compound will be bonded to a polymer system to obtain a LC elastomer with fluorescence behaviour. We can see its mechanism in **Appendix 3**.

The properties and behaviour we can observe in compound **1** or **2** that will be studied in this work are totally translatable to the compound **3**, due to their structural similarity, that will give the kick off to a new and wider study about molecular rotors and their luminescent features in different environments.

To obtain it, a Mitsunobu reaction was performed in anhydrous conditions and using THF as a solvent at room temperature.

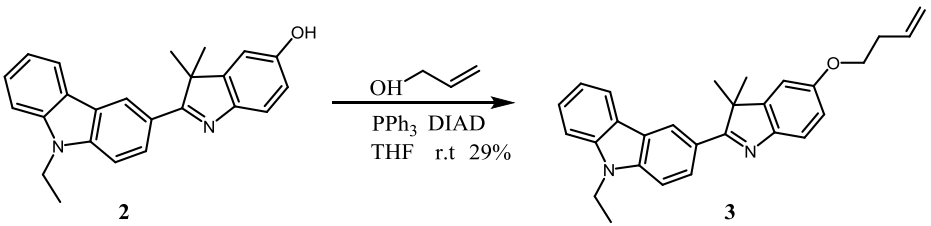


Figure 9. Synthetic procedure to obtain carbazole derivative **3**

This reaction allows the conversion of the phenol into an ether function. The nucleophile must be acidic because the DIAD needs to be protonated during the reaction to prevent it from side reactions. The triphenylphosphine combines with DIAD to generate a phosphonium intermediate that binds to the alcohol group, activating it as a leaving group. Substitution by the alcohol completes the process. [9] We can see its mechanism in **Appendix 4**. The desired product was obtained with a 29% yield.

6. CHARACTERIZATION OF THE COMPOUNDS

Compounds 1-3 have been characterized by means of the common techniques used in conventional organic synthesis, that is, ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy and Mass spectrometry. With the combination of all of them, we will be able to justify that, as it was thought, the isolated product is the correct one and they also will permit us to define whether the product is in pure conditions or has some impurity. In some cases, it can allow us to identify the impurity that is present.

6.1. Characterization of compound 1 and 2

As they both have a very similar chemical structure except from one substituent what is methoxide in compound **1** and phenol group in compound **2**, we are presenting their

characterization together to see there are the differences expected between them due to this slight difference in their structure.

6.1.1 Mass spectrometry analysis

For compound **1**, at the mass spectra (ESI), there is a peak with m/z = 369.2 that belongs to the ion $(M+H)^+$ so it suits with the expected weight of the molecule calculated $C_{25}H_{25}N_2O$ ($M+H^+$) that is 369.2 g/mol.

Referring to the compound **2**, at the mass spectra (ESI), there is a peak with m/z = 355.2 that belongs to the ion $(M+H)^+$ so it suits with the expected weight of the molecule $C_{24}H_{23}N_2O$ ($M+H^+$) that is 355.2 g/mol.

6.1.2 ^{1}H-RMN analysis

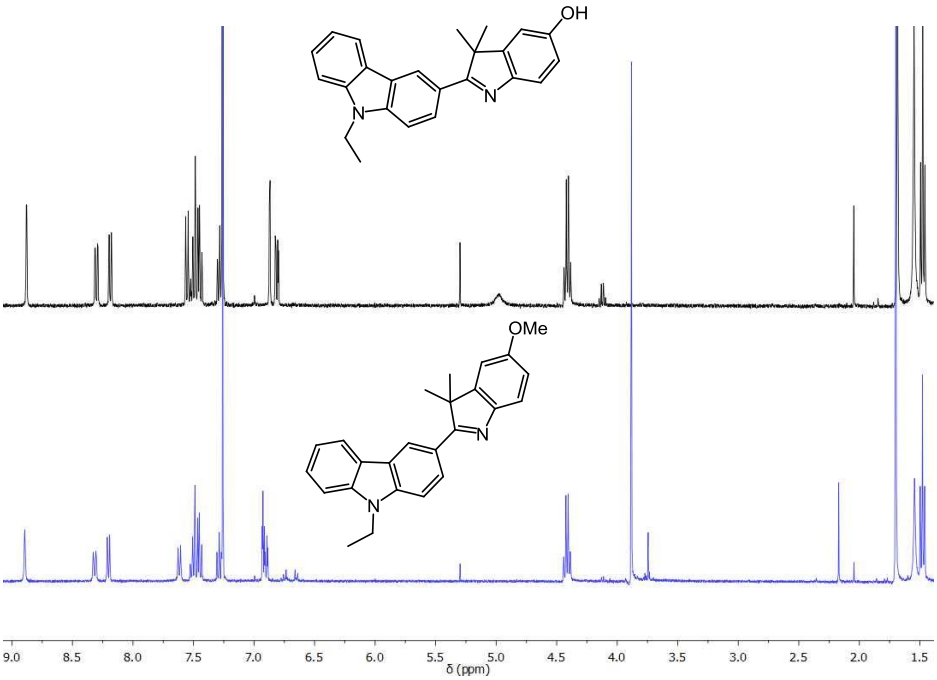


Figure 10. ^{1}H-NMR of compound **2** (black colour) and compound **1** (blue colour)

If we have into account that compound **1** and **2** are the same except from one substituent as mentioned before, the ^{1}H-NMR spectrum will be very similar one to another but with slight differences that will be discussed in the following analysis.

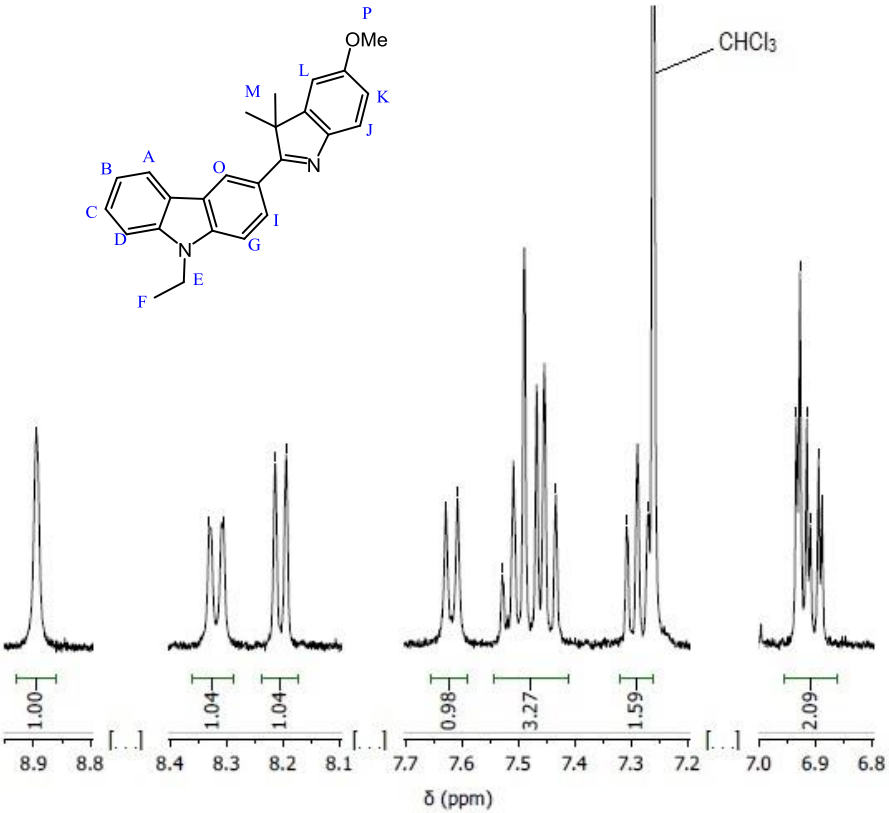


Figure 11. ^{1}H-NMR spectra for compound **1**. Aromatic side.

Observing the ^{1}H-NMR spectra, we can extract much more information that allows us to justify and realize that what we have obtained is the product expected:

The first signal we can see in the aromatic part of the spectra is a singlet at 8.90 ppm. It corresponds to the H^{O} proton as it integrates 1 proton and it cannot see any other proton due to the long bond distances. Then, we can see a doublet of doublets at 8.32 ppm and integrates 1 proton, that is H^{I} and the next one at 8.20 ppm and with integration 1 is H^{G}. We can differentiate between them because the *dd* signal must be of the first mentioned because H^{I} is giving a doublet signal with J≈ 10 Hz because the proximity and position regarding H^{G} and then a doublet inside the first one because of the coupling with H^{O} that is 4 bonds far from H^{I}.

Now, being less shielded, we have at 7.62 ppm a doublet with integration 1. It is the H^{J} because it is the only one in this region that only can couple with just one proton (H^{K}).

Next, we find a multiple signal between 7.43 and 7.53 ppm. We cannot assign exactly the H which correspond each signal but we do know that a *dd* is inside that multiple and it corresponds to H^{A}, H^{C} and H^{D} that we guess they have a doublet of doublets, doublet of doublets of doublets and another doublet of doublets respectively. Between 7.31 and 7.27 ppm we see a multiple that integrates 1H and we think it is H^{B} because it would be a doublet of doublets of doublets because it can couple first with the H^{A}, with H^{C} and with a low J with H^{D}. It is also observed another multiple between 6.89 and 6.93 ppm that we assign to H^{K} and H^{L} because they should be the most non- shielded ones. H^{K} couples with H^{J} giving a J between them of ≈10 Hz and couples with H^{L} giving a J of ≈1.5 Hz. and H^{L} should be a doublet.

This side of the spectrum is really like the aromatic part of ^{1}H-NMR of compound **1** and, there for, we would follow the same reasoning to assign the signals to the corresponding protons.

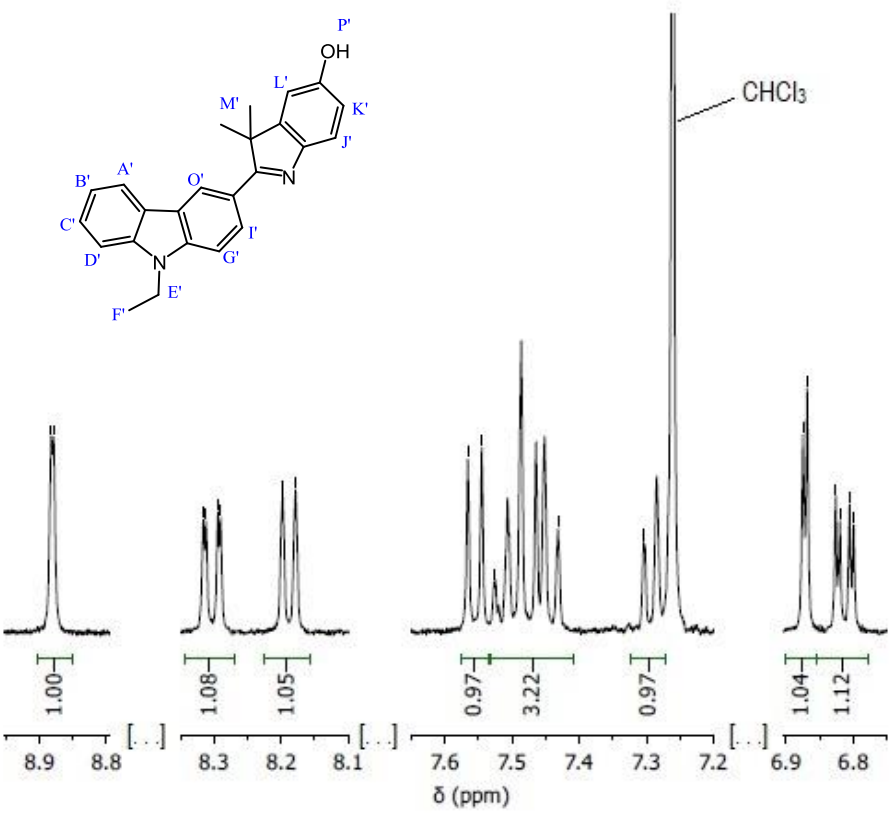


Figure 12. ^{1}H-NMR spectra for compound **2**. Aromatic side

Where we can observe the differences in the both spectra signals, is in the aliphatic part of them.

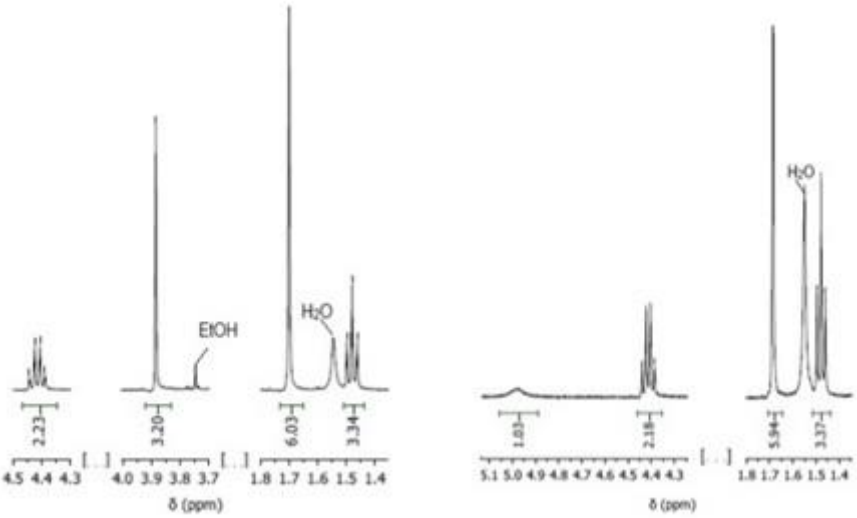


Figure 13. Aliphatic region of ^{1}H-NMR for compounds **1** (left) and **2** (right)

To assign the protons to each signal, we have chosen compound **1** to discuss the assignation due to that they will have the same reasoning for compound **2** except from two signals that are being explained later.

In this side, **figure 13** left spectrum, we observe 4 signals that suit with our thought because in the molecule we have 4 types of aliphatic H.

The first signal we observe is at 4.42 ppm that integrates 2 protons and it is a quadruplet. It belongs to H^{E} because it is the only one that can give a quadruplet as a signal because it couples with the 3H from H^{F}. Then we see a singlet that integrates 3H at 3.88 ppm that belongs to H^{P} it is the only one that can be a singlet with integration 3 because it does not couple with any other H and it is a methyl. The singlet that integrates 6H at 1.70 ppm cannot be assigned to another H but the H^{M} protons. And finally, the triplet we see at 1.48 ppm belongs to H^{F} because it couples with the 2H of H^{E} and gives a triplet as a signal and its integration is 3, because it is a methyl.

In **figure 13**, right side, we can see how compound **2** has a singlet that corresponds to the $H^{P'}$ of the alcohol group and it is at 4.80 ppm. On the other hand, the signal we had in ^{1}H-NMR

spectrum of molecule **1** belonging the H^P protons (singlet integrating 3 protons at 3.88 ppm), it is missing in the ^{1}H-NMR spectrum of the compound **2**.

6.1.3 IR spectroscopy analysis

It has been also registered an IR spectrum that shows characteristic signals that allow us to reaffirm our molecule is correct. In both we can observe the C_{sp2}-H stretching signal, at 3058 cm^{-1} for compound **1** and at 3049 cm^{-1} for compound **2**. We can also assign the C_{sp3}-H stretching signal in the two spectrums being 2981 cm^{-1} for the compound **1** and 2979 cm^{-1} for compound **2**. And, finally, as a characteristic signal we observe the C_{ar}=C_{ar} stretching at 1595 and 1469 cm^{-1} in compound **1** and at 1594 and 1459 cm^{-1} when we refer to compound **2**.

But the most important thing of the IR spectrum is to compare them to see whether we have the alcohol group in compound **2** or not.

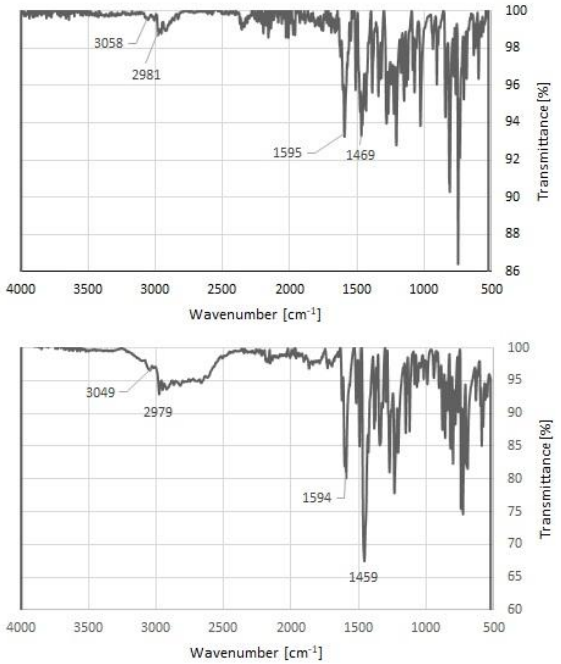


Figure 14. IR spectra for compound **1** (top) and **2** (bottom)

Effectively, we observe a wide signal around 3000 cm^{-1} that must belong to the O-H stretching.

6.2. Characterization of compound 3

For the characterization of compound **3** it is useful to compare its ^{1}H-NMR spectrum with the compound **1** one because, as it happened with the comparison between compound **1** and **2**, their spectra are very similar except from 4 new signals in compound **3** due to the chain joint to the oxygen atom instead of the methyl that was bonded in compound **1**.

6.2.1 Mass spectrometry analysis

Referring to the compound **3**, at the mass spectra (ESI), there is a peak with m/z = 411.2 that belongs to the ion $(M+H)^+$ so it suits with the expected weight of the molecule $C_{28}H_{31}N_2O$ $(M+H^+)$ that is 411.2 g/mol.

6.2.2 ^{1}H-RMN analysis

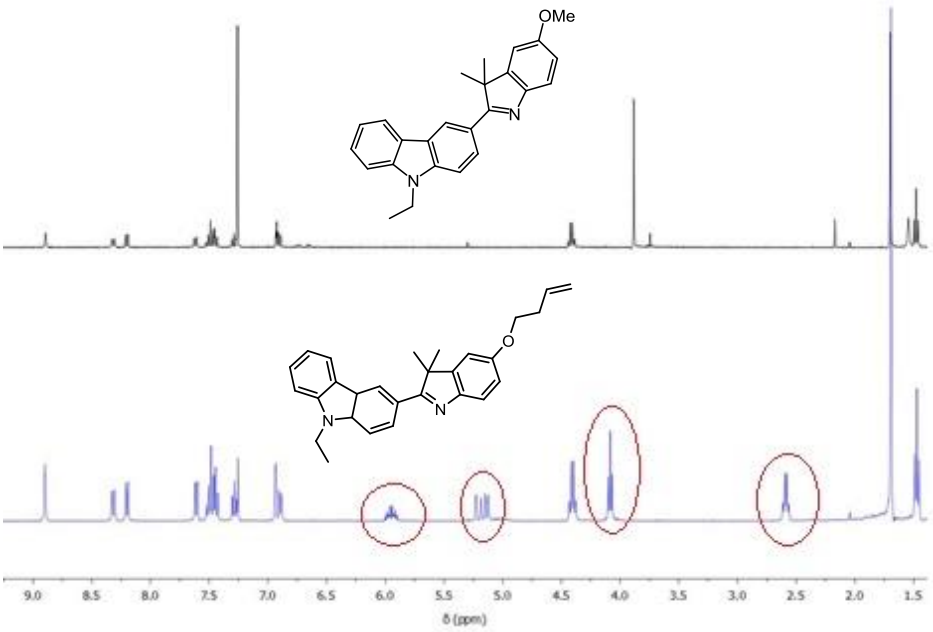


Figure 15. ^{1}H-NMR of compound **1** (black colour) and compound **3** (blue colour), where we can see the circled signals that correspond to the new ones regarding compound **1**.

There are 4 extra signals, marked in **figure 15**, although there are 5 new protons due to the added chain.

The one in 5.9 ppm belongs to H^R. this signal integrates to 1 proton and we know it is H^R because it can couple with H^{SA} in trans position, with H^{SB} in cis position, with H^Q and finally and weakly with H^P. We know that there would be a $J_{R,\ SA} \approx 16$ Hz and a $J_{R,\ SB} \approx 10$ Hz but we cannot check it because of the complexity of the multiplet signal.

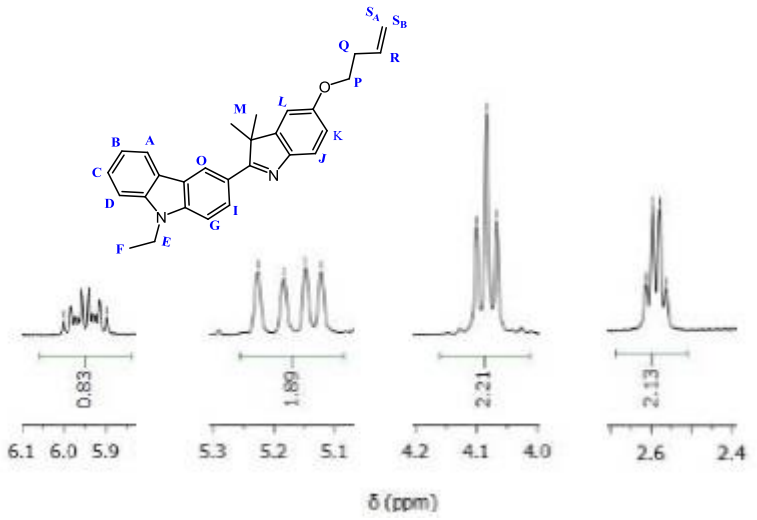


Figure 16. Enlarged aliphatic region of the ^{1}H-NMR spectrum for compound **3**

Then, we can see at 5.2ppm what seems a multiplet of 4 equal intensity signals but they are two doublets. One at 5.2ppm corresponding to H^{SA} and another at 5.1ppm that belongs to H^{SB}. We have got this resolution because of the calculus of the J constant of the first doublet, that is 17Hz and the J constant of the second doublet, that is 10Hz. So, the signal with J =17 Hz is the H^{SA} proton because it couples in trans with H^R. On the other side, the signal with J=10Hz corresponds to H^{SB} because it has a cis coupling with H^R.

At 4.08ppm we see a triplet that integrates 2 protons. It only can be H^P because it is clearly making a triplet in this region when coupling with H^Q and we do not see a triplet of doublets because $J_{P,\ R}$ is very small and we cannot see it.

Finally, we have what seems to be a quadruplet at 2.58ppm. If we think about what proton in our chain can be giving this signal, we realize there is no one that would give us a quadruplet. So, we have concluded that it is a triplet of doublets due to the coupling of H^Q with H P (triplet) and the coupling of H^Q with H^R (doublet). As they have a very similar coupling constant, signals overlap and we see an apparent quadruplet.

6.2.3 IR spectroscopy analysis

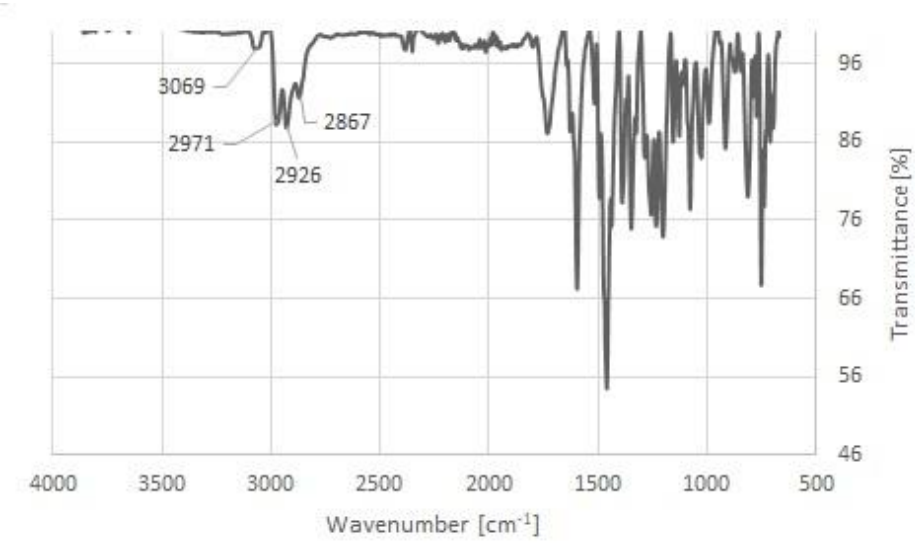


Figure 17. IR spectrum for compound **3**

There are 3 main signals in the IR spectrum that are a clear indicator of the existence of compound **3**, as it is expected.

The first one is at 3069 cm^{-1} that belongs to the stretching of the bond between C_{sp2} and Hydrogen. Then, we have a signal at 2972 cm^{-1} that is due to the stretching of C_{sp3}-H bonds. Finally, we have two characteristic signals at 1593 and 1456 cm^{-1} corresponding to the stretching of C_{AR}=C_{AR} bond.

7. PHOTO-PHYSICAL STUDY OF COMPOUNDS 1 AND 2

The compounds that are being studied photo-chemically, are expected to exhibit fluorescence within the blue region of the spectrum (400-480nm). We have studied the optical properties of these two compounds through UV-Visible and fluorescence spectroscopy.

It is known and empirically demonstrated that the more rigid, aromatic, voluminous, static and so on is the structure, the more intensity of fluorescence we might observe. But it also has a logic theoretical reasoning. Fluorescence is an emission process in which the molecules are excited by the absorption of electromagnetic radiation. The species excited, relax to the ground state releasing their excess of energy by several forms:

1. Non-radiant relaxation (it can be through vibration or internal conversion)
2. Radiant relaxation (fluorescence or, if there are crossing systems, we can get phosphorescence)

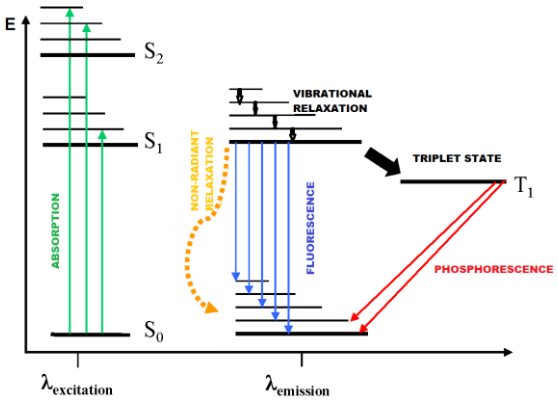


Figure 18. Simplified Jablonski diagram

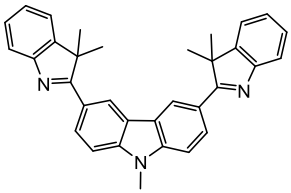
The way in which the molecule will release the excess of energy given will be determinate by the kinetic constant of each form. The shortest time it takes to leave the excited state, the better for the system. So, the molecule will relax in the way that takes shorter to get the ground state again. [10]

Then, if we raise the temperature, or decrease viscosity of the solvent, we are promoting the loss of energy by non-radiant forms thanks to the rise of collisions, vibrations and external

conversion and that, would be an explanation of why we observe less luminescence while working in certain conditions as high temperature or low viscosity environment.

The fact that the more rigidity has the compound, the more fluorescence emits, lead us to think about how we could control this variation on photo-chemical behaviour. It may exist an interrelation between the rotation state on the compound and the fluorescence it emits. [1]

We have considered a previous work done in the group to compare our results. The compound studied was **C**, **figure 19**. From that study, we have taken our hypothesis: molecular rotors increase their fluorescent activity when we increase the viscosity of the solvents where they are solved at. We also want to see the effect of the capability of stablishing hydrogen bonding. We think that, as it gives more rigidity to the system, this property will also increase the quantum yield level of the molecular rotors.



C

Figure 19. Compound **C**. The one studied in a previous work.

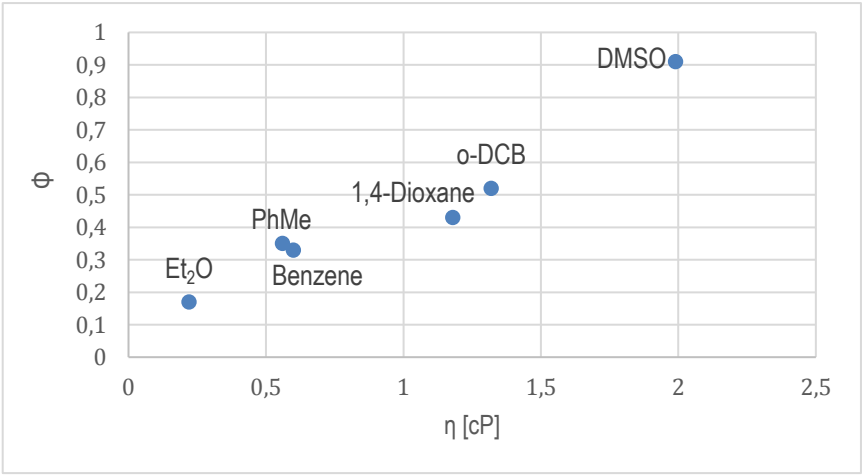


Figure 20. Fluorescent behaviour of compound **C** in different viscosity solvents

To accept or refuse the hypothesis, we are performing a photo-physical study of compounds **1** and **2** in different environments. We have studied the behaviour of our compounds in non-protic solvents to see whether they follow the tendency that we have seen in compound C, variating the viscosity of the environment, and also using solvents with protic nature maintaining this viscosity variance.

First, we have checked that our studied compounds are fluorescent in the blue region of electromagnetic spectrum. Irradiating at 350 nm.

Entry	Solvent	Absorption λ_{Abs} (ε) / nm ($mM^{-1}\cdot cm^{-1}$)		Emission λ_{Em} / nm	
		Compound 1	Compound 2	Compound 1	Compound 2
1	MeCN	347 (31)	347 (32)	430	428
2	MeOH	351 (57)	352 (26)	453	456
3	Toluene	348 (105)	347 (18)	423	420
4	EtOH	351 (28)	352 (24)	447	454
5	o-DCB	353 (27)	350 (25)	431	428
6	DMSO	353 (28)	352 (27)	433	432
7	i-PrOH	352 (33)	356 (28)	443	446
8	t-BuOH	350 (20)	350 (20)	436	436
9	BnOH	356 (16)	357 (22)	455	454

Table 1. Experimental data for absorption and emission of compounds **1** and **2**. -Solvents are organized in increasing order of viscosity level- [13]

Then, we have studied how do compounds **1** and **2** behave in different non-protic and protic solvents with different viscosity level to see whether the fact of having a phenol group or a methoxy group changes its behaviour due to the capability of stablishing hydrogen bonding easily.

To quantify the fluorescent properties of compounds we have calculated their relative fluorescence quantum yields. See **Appendix 5**.

It is calculated according to Equation 1:

$$\Phi_x = \Phi_s \cdot \frac{Abs_s}{Abs_x} \cdot \frac{n_x^2}{n_s^2} \cdot \frac{I_x}{I_s} \quad \textbf{(1)}$$

Where Abs is the absorption at the excitation wavelength, n is the refractive index of the solvent used and the I is the integrated area of the emission spectrum.

Fluorescent quantum yield (Φ) is defined as the ratio between the number of emitted photons and the photons absorbed. It gives us information about the effectiveness of the radiative decay process.

We know two ways of calculating the quantum yield of a substance [11]:

1. Calculating the absolute quantum yield. With this calculation we obtain the quantum yield by detecting all sample fluorescence using an integrating sphere.
2. Calculating the relative quantum yield. It consists of measuring the fluorescence of a compound with a known quantum yield in the same experimental conditions that we measure the fluorescence of our sample. It is much easier and cheap.

We have calculated the relative one using equation **1**. The known fluorophore used has been 9,10-Diphenylanthracene in cyclohexane, whose known absolute quantum yield is 0.95, which absorbs and emits in the same region of the electromagnetic spectrum than our compounds as it has. [12]

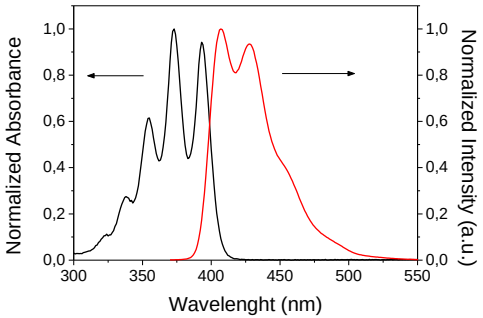


Figure 21. Normalized absorption (left) and emission (right) spectra of the standard.

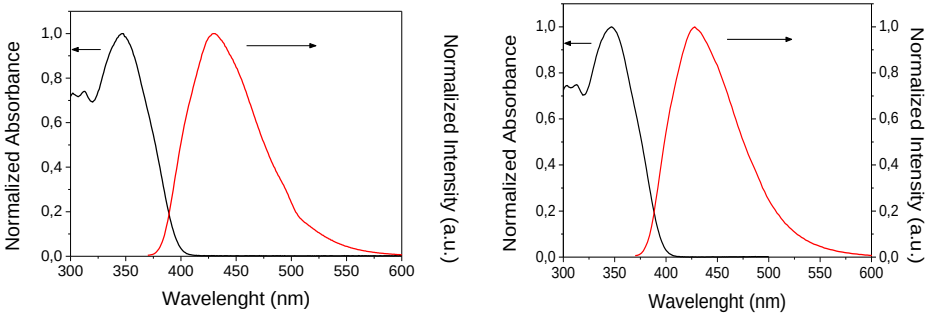


Figure 22. Normalized absorption and emission spectra of compound **1** and **2 r**espectively. In both cases, the left signal is the absorption one and the right signal is the emission one.

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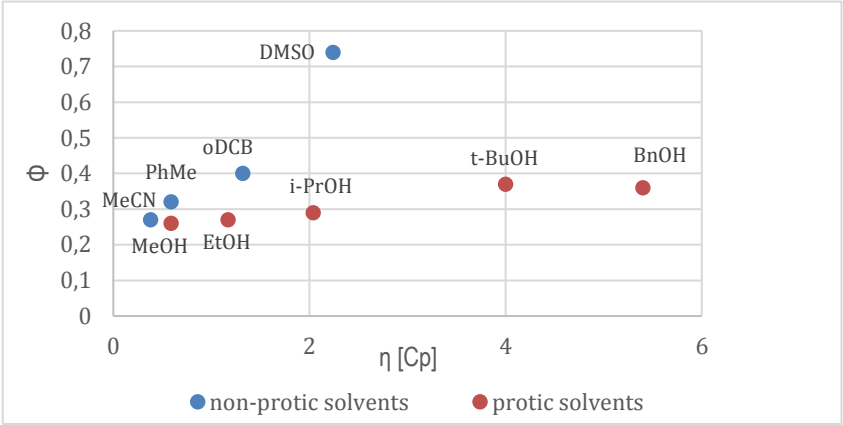


Figure 23. Tendencies of quantum yields of compound **1** when we consider different solvents.

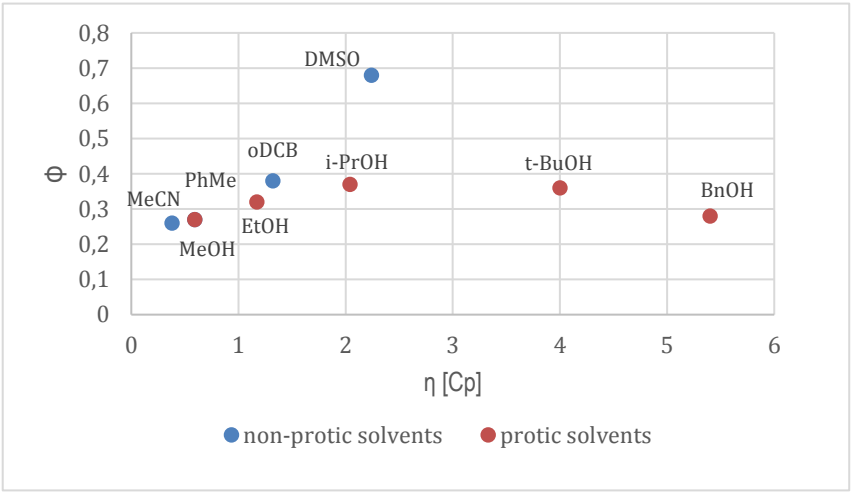


Figure 24. Tendencies of quantum yields of compound **2** when we consider different solvents.

We observe that compounds **1** and **2** behave as molecular rotors. An increment of quantum yield is observed when, in non-protic solvents, we raise the viscosity level. We see that when increasing the bulk of the protic solvent as well as its viscosity, it starts increasing the quantum yield but then it gets very similar values along the viscosity and bulk variance. They are not behaving as molecular rotors. The first part of the study suits with the previous work observation and we can say that the substituent of the molecular rotor is not determinative to make it change its fluorescent activity when being solved in protic environments.

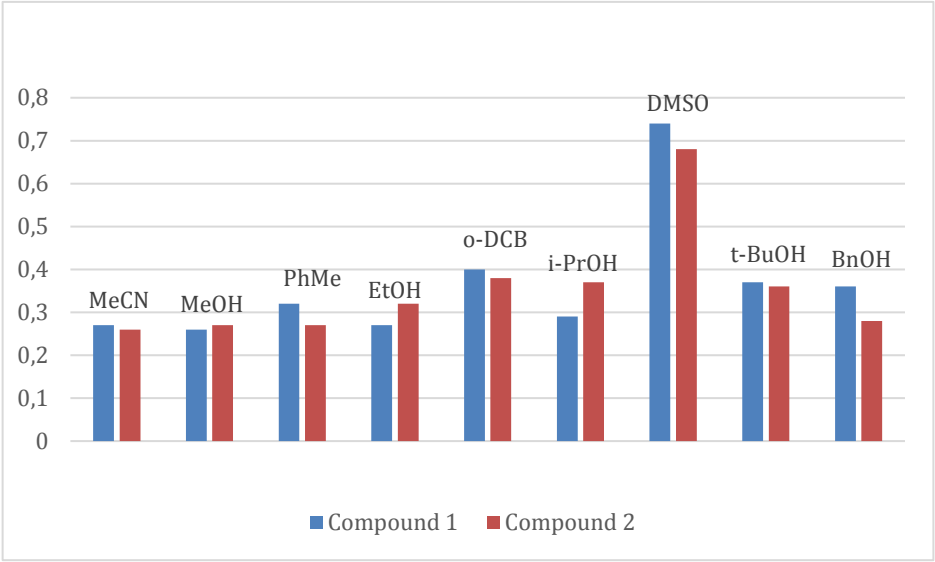


Figure 25. Comparative graphic of variance of quantum yield of compound **1** and **2** in the different solvents studied.

8. EXPERIMENT AL SECTION

8.1. MATERIALS AND METHODS

All chemicals and solvents were used as received from commercial suppliers (Sigma–Aldrich®, Panreac®) with no previous treatment. Benzene was dried over wired sodium. THF was distilled over sodium and benzophenone.

Flash column chromatography was carried out over silica gel (SDS, 230-240 mesh ASTM).

UV-Visible spectra were collected with a VARIAN CARY 500E UV-VIS-NIR spectrophotometer.

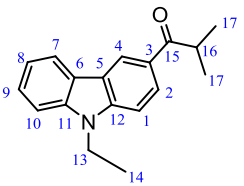
^{1}H NMR and ^{13}C NMR spectra were collected with a 400 MHz VARIAN MERCURY spectrometer.

Fluorescence spectra were registered with a PTI fluorometer, with an LPS-220B lamp and a 814 photomultiplier, equipped with the Felix 32 software and also with an Aminco-Bowman AB2 fluorometer.

8.2. PREPARATION OF 9H-CARBAZOLE DERIVATES

8.2.1. Preparation of 3-isobutyryl-9-ethylcarbazole

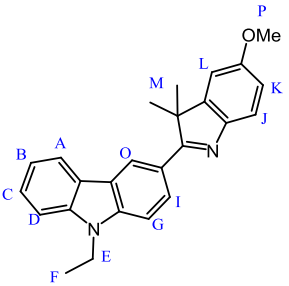
It was prepared starting from commercially available 9-ethylcarbazole (3 g, 15 mmol) and isobutyryl chloride (1.3 mL, 12 mmol) mixed, vigorously stirring, in anhydrous benzene (150 mL) at 3-8 ˚C. Aluminium chloride (2.104 g, 16 mmol) was subsequently added in small portions over a 90-min period. The resulting mixture was stirred at that temperature for an additional 30 min to finally bring it to room temperature with overnight stirring. Thereafter, the mixture was poured onto deionised water. After that, the organic extract was separated from the aqueous solution being the latter extracted with dichloromethane several times. Finally, the organic solution was distilled off under reduced pressure and purified by column chromatography, with silica-gel as stationary phase, eluting first with a 6:1 mixture of hexane and dichloromethane to end up with hexane and dichloromethane (4:1 v/v). The collected fractions of the product mixed and concentrated once it had been purified gave an oily residue.



(78% yield, 3.001 g, 8.7 mmol); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si), δ 1.30 (6 H, d, $J_{16,17}$ = 6.8 Hz, CH_3^{17}), 1.47 (3 H, t, $J_{13,14}$ = 7.2 Hz, CH_3^{14}), 3.77 (1 H, m, $J_{17,16}$ = 6.8 Hz, CH^{16}), 4.40 (2 H, q, $J_{14,13}$ = 7.2 Hz, CH_2^{13}), 7.30 (1 H, t, $J_{7,8}$ = 7.6 Hz, CH^{8}), 7.43 (1 H, d, $J_{9,10}$ = 8.4 Hz, CH^{10}), 7.45 (1 H, d, $J_{8,7}$ = 8 Hz, CH^{7}), 7.52 (1 H, t, $J_{10,9}$ = 8 Hz, CH^{9}), 8.15 (1 H, dd, $J_{4,2}$ = 1.6 Hz, $J_{1,2}$ = 8.2 Hz, CH^{2}), 8.17 (1 H, d, $J_{2,1}$ = 7.6 Hz, CH^{1}), 8.77 (1 H, d, $J_{2,4}$ =1.6 Hz, CH^{4} ppm.

8.2.2 Preparation of compound 1

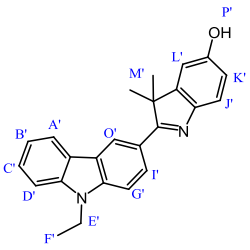
3-isobutyryl-9-ethylcarbazole (2.467 g, 9.332 mmol) is used to synthesise the indole compound dissolving it with 4-methoxyphenylhydrazine hydrochloride (1.609 g, 9.332 mmol) and 4-toluenesulfonic acid monohydrate (0.014 g, 0.139 mmol) in absolute ethanol (86 mL). Afterwards, once the solution was heated under reflux for 24 h, it was cooled down to ambient temperature to wash it with a diluted sodium bicarbonate solution followed by several extractions of the mixture with dichloromethane. The resulting organic solution was concentrated and subjected to silica-gel column chromatography starting with a mobile phase of hexane and dichloromethane (1:1 v/v) and finishing with a 2:3 mixture of hexane and dichloromethane. The corresponding fractions were concentrated later to afford the yellow solid compound **3**.



(49% yield, 1.686 g, 4.576 mmol); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si), δ 1.48 (3 H, t, $J_{F,E}$= 7.2 Hz, H^F), 1.70 (6 H, s, H^M), 3.88 (3 H, s, H^P), 4.42 (2 H, q, $J_{E,F}$= 7.2 Hz, H^E), 6.89-6.93 (2 H, m, $H^{L, H K}$), 7.31-7.27 (1 H, m, H^B), 7.43-7.53 (3 H, m, H^A, H^C, H^D), 7.62 (1 H, d, $J_{J,K}$ = 7.88 Hz H^J), 8.20 (1 H, d, $J_{G,I}$ = 7.92 Hz, H^G), 8.32 (1 H, dd, $J_{I,G}$= 10,2 Hz, H^I), 8.90 (1 H, s, H^O) ppm. **^{13}C NMR** (100 MHz; $CDCl_3$; Me_4Si), δ 13.85, 25.60, 37.73, 53.59, 55.74, 107.61, 108.36, 108.78, 112.30, 119.52, 120.54, 120.70, 123.06, 123.23, 124.35, 126.09, 126.14, 140.44,141.05, 149.33, 158.07, 182.01 ppm. **MS** (ESI): m/z calculated for $C_{25}H_{25}N_2O$ $(M+H)^+$, 369.2, experimental m/z for $C_{25}H_{25}N_2O$ $(M+H)^+$, 369.2. **IR** (ATR FT-IR): 3058 (Csp_2-H st.), 2981 (Csp_3-H st.), 1595 and 1470 (Car=Car st.) cm^{-1}.

8.2.3 Preparation of compound 2

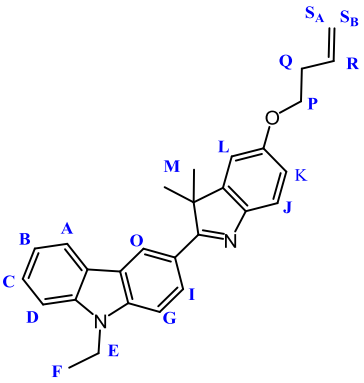
To achieve the deprotection reaction of *O*-demethylation, a solution of BBr3 (1 M, 7 mL, 7.3 mmol) in dichloromethane was added dropwise to a solution of **1** (1.621 g, 4.405 mmol) in anhydrous dichloromethane under nitrogen atmosphere at 0 ºC and stirred for 1 h. Then, the mixture was warmed up to ambient temperature and maintained under these conditions for 14 h. Finally, the product was isolated by washing the organic layer with a saturated sodium bicarbonate solution and extracting the mixture with dichloromethane, and subsequently concentrated and eluted in a silica-gel column chromatography using ethyl acetate and dichloromethane mixture (95:5 v/v. Once purified, the fractions were distilled off under reduced pressure to obtain the 3-(5-hydroxy-3,3-dimethyl-3*H*-indol-2-yl)-9-ethylcarbazole, **2**.



(51% yield, 0.788 g, 2 mmol); **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si), δ 1.48 (3 H, t, $J_{F',E'}$ = 7.2 Hz, H^{F}), 1.69 (6 H, s, H $^{M'}$), 4.41 (2 H, q, $J_{E',F'}$ = 7.2 Hz, $H^{E'}$), 4.97 (1 H, s, $H^{P'}$), 6.81 (1 H, dd, $J_{K',J'}$ = 8.2 Hz, $J_{K',L'}$= 2.5 Hz, $H^{K'}$), 6.87 (1 H, d, $J_{L',K'}$ = 2.5 Hz, $H^{L'}$), 7.3-7.26 (1 H, m, $H^{B'}$), 7.43-7.53 (3 H, m, $H^{A'}$, $H^{C'}$, $H^{D'}$), 7.55 (1 H, d, $J_{J',K'}$ = 8.2 Hz, $H^{J'}$), 8.19 (1 H, d, $J_{G',I'}$ = 7.8 Hz, $H^{G'}$), 8.30 (1 H, dd, $J_{I',O'}$ = 1.7 Hz, $J_{I',G'}$ = 8.8 Hz, $H^{I'}$), 8.88 (1 H, d, $J_{O',I'}$ = 1.4 Hz, $H^{O'}$) ppm.
^{13}C NMR (100 MHz; DMSO-d6; Me_4Si), δ 14.18, 25.42, 37.57, 53.21, 55.34, 109.10, 109.65, 109.83, 114.36, 119.75, 120.44, 120.64, 121.30, 122.67, 122.92, 124.45, 126.33, 126.60, 140.46, 140.87, 145.77, 150.06, 156.18, 180.32 ppm. **MS** (ESI): m/z calculated for $C_{24}H_{23}N_2O$ ($M+H^+$), 355.2. Experimental m/z for $C_{24}H_{23}N_2O$ ($M+H^+$), 355.2. **IR** (ATR FT-IR): 3200-2500 (O-H st.), 3049 (Csp_2-H st.), 2979 (Csp_3-H st.), 1594 and 1460 (Car=Car st.) cm^{-1}.

8.2.4 Preparation of compound 3

The *O*-alkylation was achieved through a Mitsunobu reaction. Compound 2 (0.250 g, 0.678 mmol) and triphenylphosphine (0.178 g, 0.678 mmol) were mixed in anhydrous THF (50 mL) under nitrogen atmosphere at room temperature. Afterwards, di-isopropyl azodicarboxylate (DIAD) (0.130 mL, 0.678 mmol) and 3-buten-1-ol (0.05 mL, 0.581 mmol) were added to the mixture, subsequently stirred for 24h. Finally, the product was concentrated under reduced pressure and eluted with a mobile phase of hexane and dichloromethane (1:4 v/v). The fluorophore obtained presented a yellow-green oily aspect.



(29% yield, 0.08 g, 0.204 mmol. **^{1}H NMR** (400 MHz; $CDCl_3$; Me_4Si), δ 1.47 (3 H, t, $J_{F,E}$= 7.2 Hz, H^F), 1.69 (6 H, s, H^M, 4.08 (2 H, t, $J_{P,Q}$ = 6.4 Hz, H^P), 4.41 (2 H, q, $J_{E,F}$ = 7.2 Hz, H^E), 6.89 (1 H, dd, $J_{K,J}$ = 8.4 Hz, $J_{K,L}$ = 2 Hz, H^K), 6.94 (1 H, d, $J_{L,K}$ = 2.4 Hz, H^L), 7.26-7.3 (1 H, m, H^B), 7.43-7.52 (3 H, m, H^A, H^C, H^D), 7.61 (1 H, d, $J_{J,K}$ = 8.4 Hz, H^J), 8.20 (1 H, d, $J_{G,I}$ = 7.6 Hz, H^G), 8.32 (1 H, d, $J_{I,G}$ = 8.8 Hz, H^I), 8.89 (1 H, s, H^O) ppm. **^{13}C NMR** (100 MHz; $CDCl_3$; Me_4Si), δ 13.83, 25.58, 29.66, 33.77, 37.70, 53.56, 67.74, 108.34, 108.75, 112.97, 117.00, 119.48, 120.50, 120.66, 123.05, 123.21, 126.08, 126.12, 134.50, 140.42, 141.04, 149.27, 157.38, 181.98 ppm. **MS** (ESI): m/z calculated for $C_{28}H_{31}N_2O$ ($M+H^+$), 411.2. Experimental m/z for $C_{28}H_{31}N_2O$ ($M+H^+$), 411.2. **IR** (ATR FT-IR): 3069 (Csp_2-H st.), 2972 (Csp_3-H st.), 1593 and 1456 (Car=Car st.) cm^{-1}.

9. CONCLUSIONS

The main conclusions of the present study can be summarized as follows:

- A synthetic pathway to obtain the desired compounds**1**-**3** has been followed and these compounds have been successfully synthetized and characterized by the usual techniques used within organic synthesis.
- Compounds **1** and **2** behave as molecular rotors. Their resistance to rotate on themselves is related to the fluorescent activity they have. They present an incrementation of fluorescence activity when increasing the viscosity of the non-protic solvents where they are solved at.
- Compounds **1** and **2** do not behave as molecular rotors when we talk about protic solvents. We have concluded that the increasing tendency observed before is not valid anymore. There is some other fact, related to the use of protic solvents that disturbs that tendency. Similar quantum yield are determined in all the protic solvents used. The studied molecular rotors do not present any clear dependence neither on the viscosity level of the environment nor the ramification of C^{α} in protic solvents. Its dependence is anomalous.
- When wondering whether they are suitable or not for the desired applications such as being emitters in the polymer system, we can say that the synthetized products are good fluorophores that respond to variance of viscosity level in the environment and are photo-physically active in the blue region of the electromagnetic spectrum only when they are introduced in non-protic environments.

10.REFERENCES AND NOTES

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11. ACRONYMS, ABBREVIATIONS AND SYMOBOLS

^{1}H NMR	^{1}H nuclear magnetic resonance
Φ_{ref}	Absolute quantum yield of the reference
Abs	Absorbance
Abs_s	Absorbance of the reference
Abs_x	Absorbance of the sample
λ_{Abs}	Absorbance wavelength
BnOH	Benzyl alcohol
cP	Centipoises
δ	Chemical shift
J	Coupling constant
DIAD	Diisopropyl azodicarboxylate
DMSO	Dimethyl Sulfoxide
d	Doublet
dd	Doublet of doublets
ESI	Electrospray ionisation
$\lambda_{emission}$	Emission wavelength
E	Energy
$\lambda_{excitation}$	Excitation wavelength
Φ	Fluorescence quantum yield
IR	Infrared spectroscopy
I	Integrated area of the emission spectrum
I_x	Integrated area of the sample emission spectrum
I_s	Integrated area of the standard emission spectrum
LC	Liquid crystal
LSCE	Liquid single-crystal elastomer
m/z	Mass to charge ratio
ε	Molar extinction coefficient
m	Multiplet
o-DCB	*o*-Dichlorobenzene
ppm	Parts per million
TsOH	*p*-Toluenesulfonic acid
n_{ref}	Refractive index of the reference
n_{sample}	Refractive index of the sample
Φ_{sample}	Relative quantum yield of the sample
r.t.	Room temperature
s	Singlet
S_1	Singlet first excited electronic state
S_0	Singlet ground electronic state
S_2	Singlet second excited electronic state
st	Stretching
THF	Tetrahydrofuran
t	Triplet

T_1	Triplet excited electronic state
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
η	Viscosity
λ	Wavelength

APPENDICES

APPENDIX 1: Reaction mechanism for the formation of 3-isobutyryl-9-ethylcarbazole

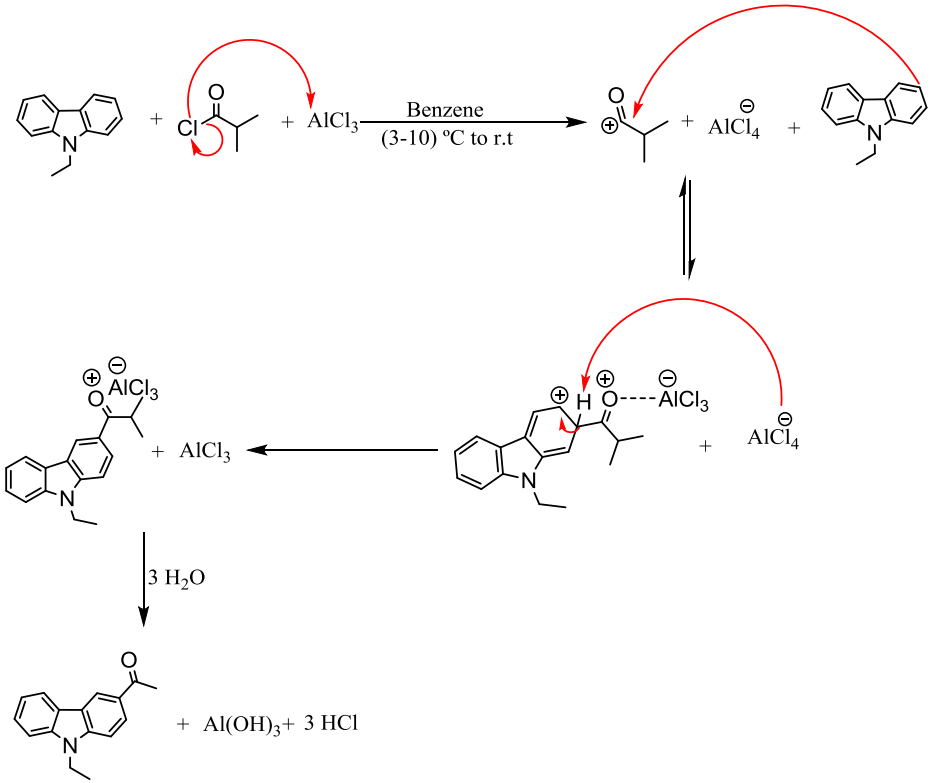

Figure A1. Reaction mechanism for the formation of 3-isobutyryl-9-ethylcarbazole

APPENDIX 2: Reaction mechanism for the formation of compound 1

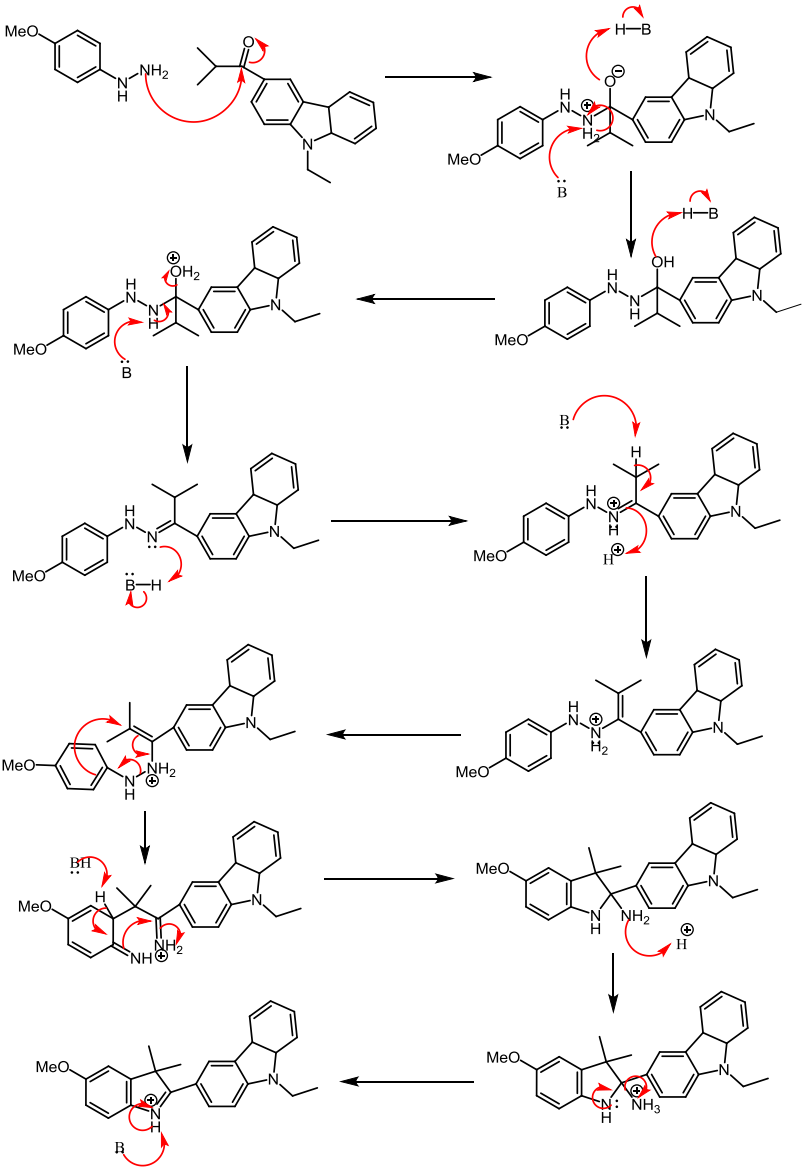

Figure A2. Reaction mechanism for the formation of compound **1**.

APPENDIX 3: Reaction mechanism for the formation of compound 2

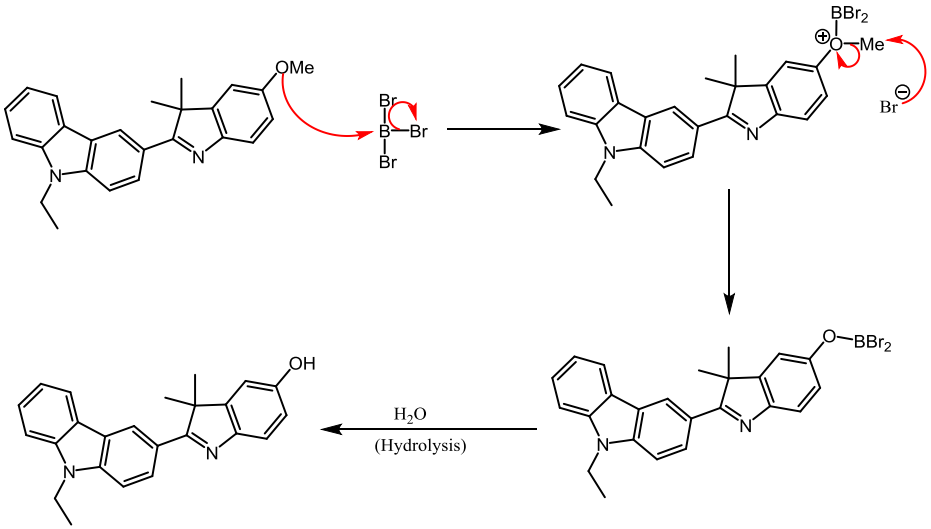

Figure A3. Reaction mechanism for the formation of compound **2**.

APPENDIX 4: Reaction mechanism for the formation of compound 3

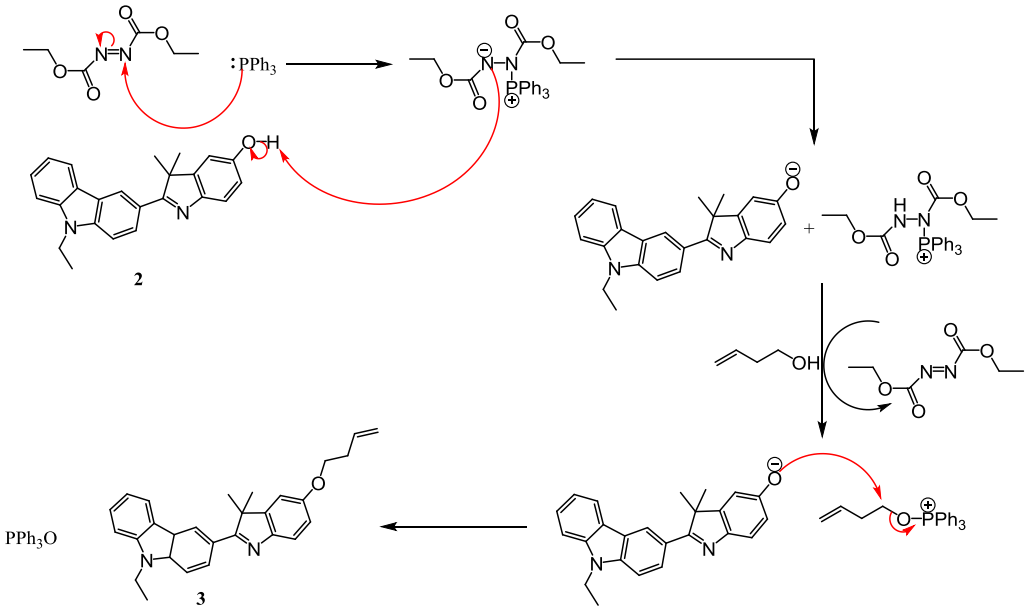

Figure A4. Reaction mechanism for the formation of compound **3**.

APPENDIX 5: EXPERIMENTAL DATA FOR Φ CALCULATION.

Solvent	Compound	Viscosity η [cP]	Absorption Abs at 350nm	Emission I (I$_s$)	Relative quantum yield (Φ)
MeCN	**1**	0.38	0.0501	1433 (4283)	0.27
	2		0.0503	25411800 (90149800)	0.26
MeOH	**1**	0.59	0.0513	1422 (4283)	0.26
	2		0.0532	28020700 (90149800)	0.27
Toluene	**1**	0.59	0.0513	1370 (4282)	0.32
	2		0.0576	24215500 (90149800)	0.27
EtOH	**1**	1.17	0.0534	919 (2823)	0.27
	2		0.0552	34689200 (91922100)	0.32
o-DCB	**1**	1.32	0.0501	959 (2807)	0.4
	2		0.0491	27164100 (90149800)	0.38
Isopropanol	**1**	2.04	0.0534	954 (2823)	0.29
	2		0.0476	32857800 (90149800)	0.37
DMSO	**1**	2.24	0.0516	1994 (2807)	0.74
	2		0.0546	59459600 (90149800)	0.68
t-BuOH	**1**	4	0.0587	39976400 (90149800)	0.37
	2		0.0524	34064000 (90149800)	0.36
Benzyl alcohol	**1**	5.4	0.0492	1420 (4282)	0.36
	2		0.0519	22905200 (97190300)	0.28

Figure A5. Experimental data for Φ calculation.