

THE SYNTHESIS OF TUNABLE PUSH-PULL  
BENZOFULVENE MONOMERS

by

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A THESIS

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## **An Abstract of the Thesis of**

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Primary Thesis Advisor

Researchers are increasingly aware of the unique optical properties and customizability of benzofulvenes, features that lend themselves to a variety of applications in optoelectronics and other fields. This research tested a simple and mild synthetic route, producing a wide range of functionalized benzofulvenes using phenyl indene intermediates. Benzofulvene structures were confirmed with NMR and optical data was collected using UV-vis spectroscopy and fluorimetry. It was found that strong electron push-pull systems, especially those involving a trifluoromethyl withdrawing group, experienced the most red-shifting. Solvents were also found to influence absorption wavelengths and emission intensity. Thus, benzofulvenes made with this method are tunable – substituents and solvents can easily be combined in unique ways to produce a variety of colors and fluorescence effects.

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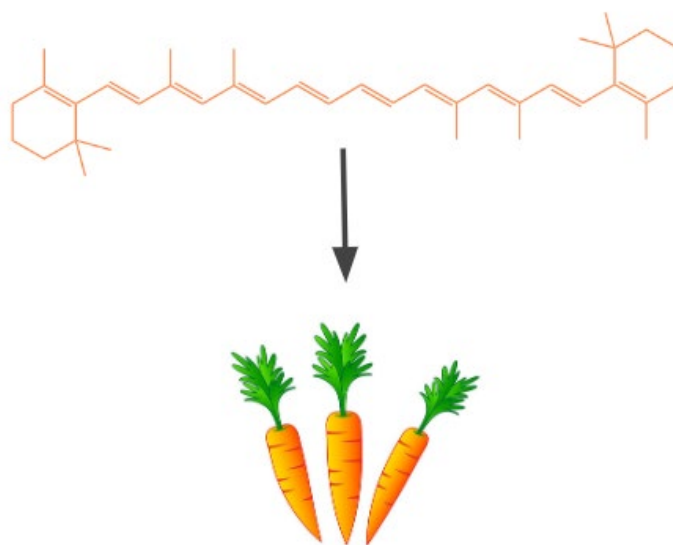
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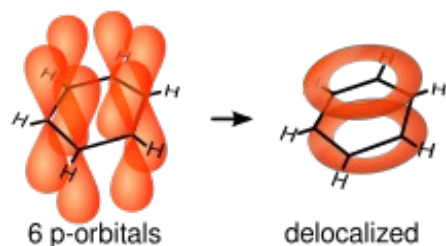
## Introduction

### Conjugation and Aromaticity

A common phenomenon in organic chemistry is the ‘linking together’ of double bonds between atoms in a molecule, which is known as *conjugation*. The entire chain, or ring in some cases, of double bonds is called a pi system. The significance of conjugation is that it makes a molecule more stable.<sup>1</sup> The term *orbital* is used to describe a region around an atom or molecule where electrons are likely to be found. In the case of a pi system, the *p orbitals* (a type of atomic orbital) of all of the atoms participating in a double bond laterally overlap with each other, allowing electrons to travel throughout the entire system. Colorful compounds, such as those in carrots and eggplants, contain extensive pi systems which can absorb light of certain wavelengths. Shown in Figure 1 is carotene, a major pigment in carrots, which appears orange because the pi system absorbs blue-green light, thus the *remaining* light reflected into our eyes is orange.<sup>2</sup>

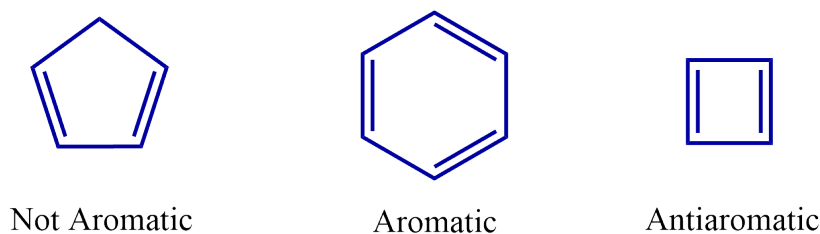


**Figure 1.** The beta-carotene pigment gives carrots their orange color. (Liu, 2019)



**Figure 2.** Benzene displays aromaticity, a special type of conjugation where electrons in p orbitals can delocalize around the entire ring. (Liu, 2019)

One type of conjugation characterized by particularly high stability is *aromaticity*. To be aromatic, a molecule must adhere to several criteria. Firstly, it must be cyclic, so that delocalized pi electrons can spread out across a ring (or multiple rings). This ties into the second factor, which is that conjugation of p orbitals must occur throughout the entire ring, as seen in Figure 2. Thirdly, the molecule must follow Hückel's rule, meaning that it should have  $4n + 2$  pi electrons (where n is an integer).<sup>3</sup> If there are  $4n$  pi electrons, however, then the compound is *antiaromatic* and therefore highly *unstable*.<sup>4</sup> Figure 3 below provides some examples of cyclic molecules with varying aromaticities.



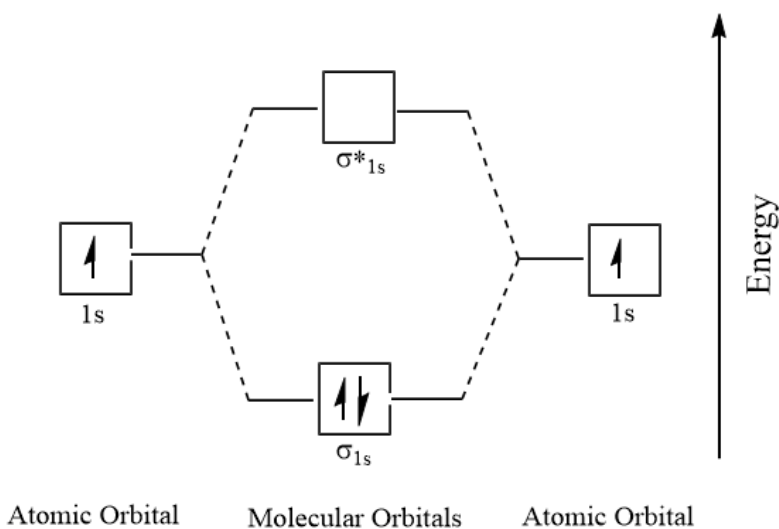
**Figure 3.** Cyclopentadiene (left) is non-aromatic due to the ring not being fully conjugated, while cyclobutadiene (right) is antiaromatic due to having 4 pi electrons. (Ashenhurst, 2017; Madhusa, 2018)

### Molecular Orbital Theory

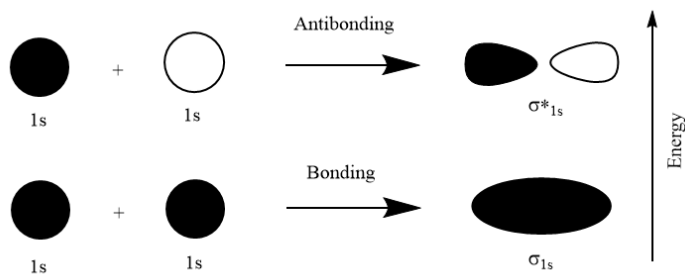
An essential concept in understanding conjugation and other bonding patterns is molecular orbital (MO) theory, wherein atomic orbitals (regions of electron density around an atom) combine to form molecular orbitals (patterns of electron density between atoms in the



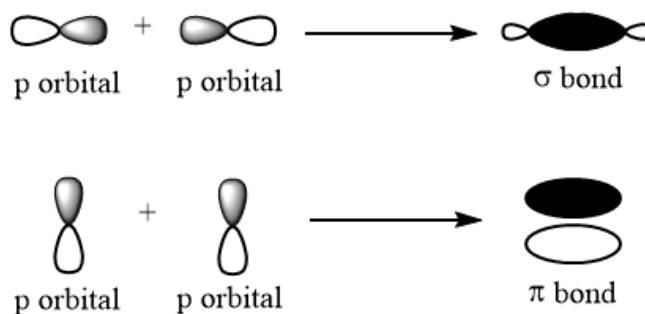
same molecule).<sup>5</sup> When atoms interact, the wave functions of their orbitals can constructively or destructively interfere, creating stable bonding MOs and unstable antibonding MOs, respectively.<sup>5</sup> Both atomic and molecular orbitals follow the Aufbau principle, where electron filling occurs from lowest-energy to highest-energy states, and the Pauli exclusion principle, where each orbital can contain up to 2 electrons with opposing spins.<sup>5</sup> The formation of MOs can be seen in Figure 4 below.



**Figure 4.** An MO energy diagram for H<sub>2</sub>, where atomic s orbitals of hydrogen atoms combine to form molecular orbitals. Arrows represent individual electrons, and  $\sigma_{1s}$  (a bonding MO) fills with electrons before the higher energy  $\sigma^*_{1s}$  (an antibonding MO) can. (Key, 2014)



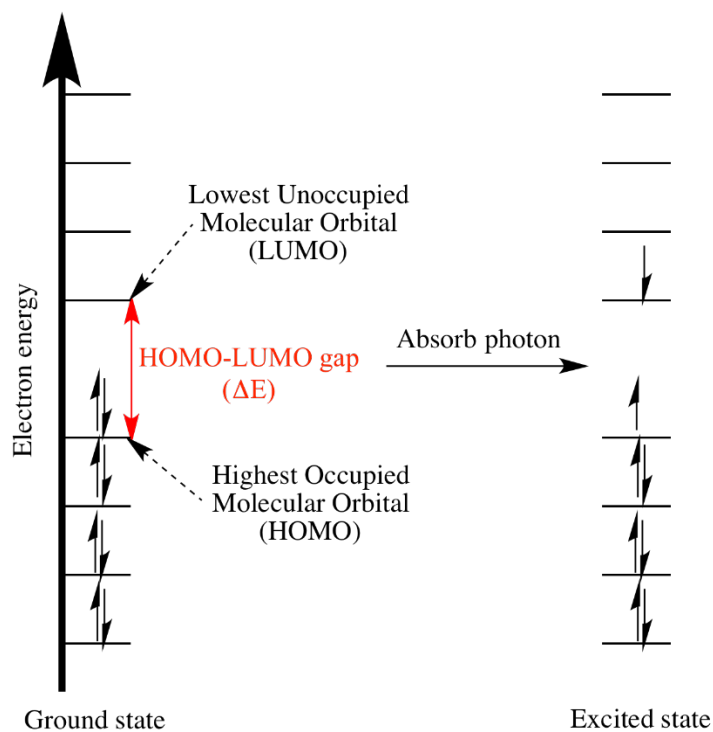
**Figure 5.** Atomic orbitals that are in phase form low-energy bonding MOs, while out-of-phase orbitals form high-energy antibonding MOs. (Key, 2014)



**Figure 6.** Direct and lateral overlapping of atomic p orbitals form sigma and pi bonding MOs (when in phase), respectively. (Farmer et al., n.d.)

Different types of atomic orbitals can combine to form different MOs, as shown in Figures 4-6. While s orbitals only form sigma bonds, p orbitals can form sigma or pi bonds depending on orientation, the latter of which is required for conjugated systems.<sup>6</sup>

Frontier molecular orbitals are often involved in forming chemical bonds, particularly pi bonds. They include the highest occupied molecular orbital (HOMO), the highest-energy molecular orbital containing electrons, and the lowest unoccupied molecular orbital (LUMO), the lowest-energy molecular orbital without electrons. Since electrons fill orbitals at low to high energies, the HOMO is energetically right underneath the LUMO.<sup>7</sup> Upon absorption of a photon, one electron is excited from the HOMO to the LUMO, as shown in Figure 7 below. The energy gap between the frontier molecular orbitals determines the energy level (and thus, the wavelength) of the photon needed to excite the electron. Highly conjugated molecules tend to have smaller HOMO-LUMO gaps, meaning that they can absorb photons with longer wavelengths.<sup>8</sup> UV-Vis spectroscopy, a technique where UV and visible light is separated into their constituent wavelengths by diffraction grating and then shone through a compound dissolved in a colorless solvent, can be used to compare the absorption maxima of similar molecules. A bathochromic or “red” (increased wavelength) shift in absorption maxima is characteristic of strong conjugation.<sup>9</sup>

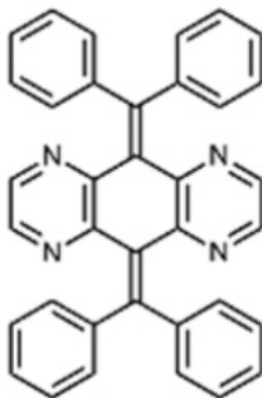


**Figure 7.** Absorption of a photon can cause an electron to ‘jump’ in energy from the HOMO to the LUMO. (Illustrated Glossary of Organic Chemistry, n.d.)<sup>10</sup>

## Optoelectronic Applications

The field of optoelectronics contains relevant applications for conjugated molecules, with applications including OLEDs, color-changing electrochromic devices, and photovoltaic cells. Conjugated polymers are widely used in OLED technology due to their semiconductive properties, ease of processing, and ability to emit a broad spectrum of light wavelengths.<sup>11</sup> A less-studied alternative to polymers are conjugated small molecules (such as monomers), which are advantageous in their ease of synthesis, addition of functional groups, purification with standard techniques, and control of material properties.<sup>12</sup> An additional quality necessary for a molecule to be useful in optoelectronics is *tunability*. An example of this is molecular switches, compounds whose structures can be altered by an external stimulus. Breakthroughs are being made in research following molecules called anthraquinodimethanes (AQDs), which have been found to have several different forms, each emitting different wavelengths of light (i.e. colors).<sup>13</sup>

One such molecule is shown in Figure 8. A molecular switch involving this compound could allow its color to be controllable, giving it a new range of applications in the field of optoelectronics.



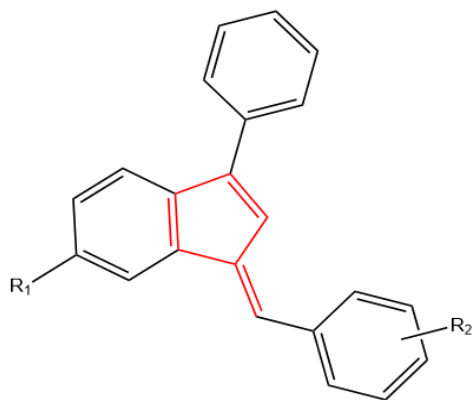
**Figure 8.** A derivative of tetraaryl-AQD, a type of AQD synthesized by Sugawara et al. (2023)

### **Fulvenes and Benzofulvenes**

Fulvenes (particularly pentafulvenes) are molecules with a wide variety of applications in chemistry, including interactions with metals and synthesis of biologically relevant molecules. They also have unique photophysical and nonlinear optical properties, as well as displaying a quality called an “aromatic chameleon”.<sup>14</sup> This means that fulvenes can switch between aromatic and antiaromatic based on whether they are in the singlet state or the excited triplet state, which relates to the respective absence or presence of unpaired electrons. The aromaticity of fulvene in each state could also be manipulated by the addition of certain substituents, affecting the amount of energy required to transition a fulvene molecule into the triplet state.<sup>15</sup> Transitioning between triplet and singlet states is an essential component of phosphorescence, which may thus be another possible application of fulvenes.<sup>16</sup> Of particular relevance, however, is the fact that certain fulvenes contain a relatively small HOMO-LUMO gap, allowing them to absorb long-wave UV light and appear yellow-red in color. The HOMO-LUMO gap can also be tuned by

placing different substituents on the fulvene molecule, resulting in different wavelengths that can be absorbed.<sup>17</sup> For example, the addition of an electron *withdrawing* group to the exocyclic carbon lowers the energy gap, meaning that a lower-energy photon is needed to excite an electron in the fulvene, thereby “red-shifting” the molecule. As a result, the color of fulvenes can be manipulated.

Benzofulvenes (see Figure 9) are larger molecules containing fulvene that are well known for their role in materials science, medicine, and photovoltaics.<sup>18–20</sup> They contain relatively large conjugated pi systems and can be divided into central indene and exocyclic aromatic moieties, each of which can be functionalized with different groups.<sup>21</sup> This means that benzofulvenes have just as much if not more potential for customization than fulvenes alone.



**Figure 9.** Benzofulvene with a pentafulvene ‘core’ in red, where R groups represent a substituent and a general customization of the benzene ring, respectively. It contains an indene moiety (left side) and a exocyclic aromatic portion (lower-right side). (Glass et al., 2018)

Like fulvenes, benzofulvenes can be optically excited relatively easily due to possessing small HOMO-LUMO gaps. Absorbance can be manipulated via the addition of substituent groups, though the range of colors and tunability have yet to be fully explored.<sup>17</sup> As molecules of increasing popularity due to their applications and unique properties, finding ways to synthesize benzofulvenes and their derivatives has been the focus of many researchers in recent years.

Several synthetic pathways have been proposed, though most of them tend to be complicated and involve expensive reactants and difficult-to-produce intermediates.<sup>21</sup> This project focuses on a short and relatively mild synthetic route to benzofulvenes proposed and optimized by our research group in previous work<sup>21</sup>, with the aim of testing its ability to produce a wide variety of functionalized benzofulvenes with a range of HOMO-LUMO gaps and absorption wavelengths (resulting in a range of colors). If proven useful, this research could be published so that our synthetic pathway can be further studied and improved upon by other scientists, as well as utilized by engineers in optoelectronics and other relevant fields.

## Methods

### General Overview of Methods

#### *Column Chromatography*

Column chromatography is used to isolate a desired compound out from a solution. Solutes of differing polarity experience different degrees of attraction to the highly polar stationary phase and thus travel through the column at different rates. The eluate is collected over time using multiple test tubes, a short range of which will contain a majority of the desired compound. An eluent of 90:10 hexanes:EtOAc was used except in cases of poor separation, where a more polar eluent was pursued. Dry-loading was often done to improve separation. TLC was used to test eluate samples for presence and purity of the desired product.

#### *<sup>1</sup>H NMR Spectroscopy*

This procedure is used to detect the presence of different molecular components and functional groups, thereby determining whether the desired product was synthesized. Samples from each compound were purified, dissolved in 800  $\mu$ L of deuterated chloroform, and transferred into an NMR tube. NMR spectra were obtained using a Bruker Avance III HD spectrometer.

#### *Crystallography*

X-ray crystallography is used to determine diffraction intensities of benzofulvene crystal structures. A layer of dissolved benzofulvene was added to a labeled septum vial with a needle to allow for slow evaporation of the solvent, resulting in the precipitation of fluorescent crystals. Diffraction intensities were obtained using a Bruker Apex2 DUO CCD diffractometer at 173 K using Cu K- $\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$ . Absorption corrections were made using SADABS5.

### *UV-Vis Spectroscopy*

Ultraviolet-visible (UV-vis) spectroscopy tests the degree to which a compound absorbs a spectrum of light wavelengths in the UV-visible range. An Agilent Technologies Cary 60 UV-Vis spectrophotometer was used with Cary WinUV Scan. Absorbance spectra for each compound were collected from 300 nm to 600 nm. To test solvatochromism, absorbance spectra were also taken of selected compounds dissolved in hexanes, chloroform, ethyl acetate, DMSO, and DMF.

### *Fluorimetry*

Fluorescence spectroscopy, or fluorimetry, is used to determine patterns of fluorescence in a compound after being excited by a specific photon. A Horiba Jobin Yvon Fluoromax-4 spectrofluorometer was used with FluorEssence. Emission spectra for selected compounds were collected from  $\lambda_{\text{max}} + 5$  nm up to 700 nm.

### *Aggregation-Induced Emission (AIE)*

AIE involves the addition of (deionized) water to a dissolved product to form a colloidal nanoparticle solution (i.e. a suspended solid). This prevents solvation and restricts rotation of the exocyclic aromatic hydrocarbon, resulting in increased fluorescence. Emission spectra were taken for selected compounds in DMF and DMSO using the following volumes of water: 100  $\mu\text{L}$ , 300  $\mu\text{L}$ , 900  $\mu\text{L}$ , 3000  $\mu\text{L}$ , and 8000  $\mu\text{L}$ .

### **General Synthesis of Indene Precursors**

Firstly, a magnetic stir bar and a septum are added onto a warm 25-50 mL round-bottomed flask (RBF). Using a Schlenk Line, any atmospheric air and water vapor are removed under reduced pressure for 5 minutes. Then, the flask is flushed with dry nitrogen gas. The

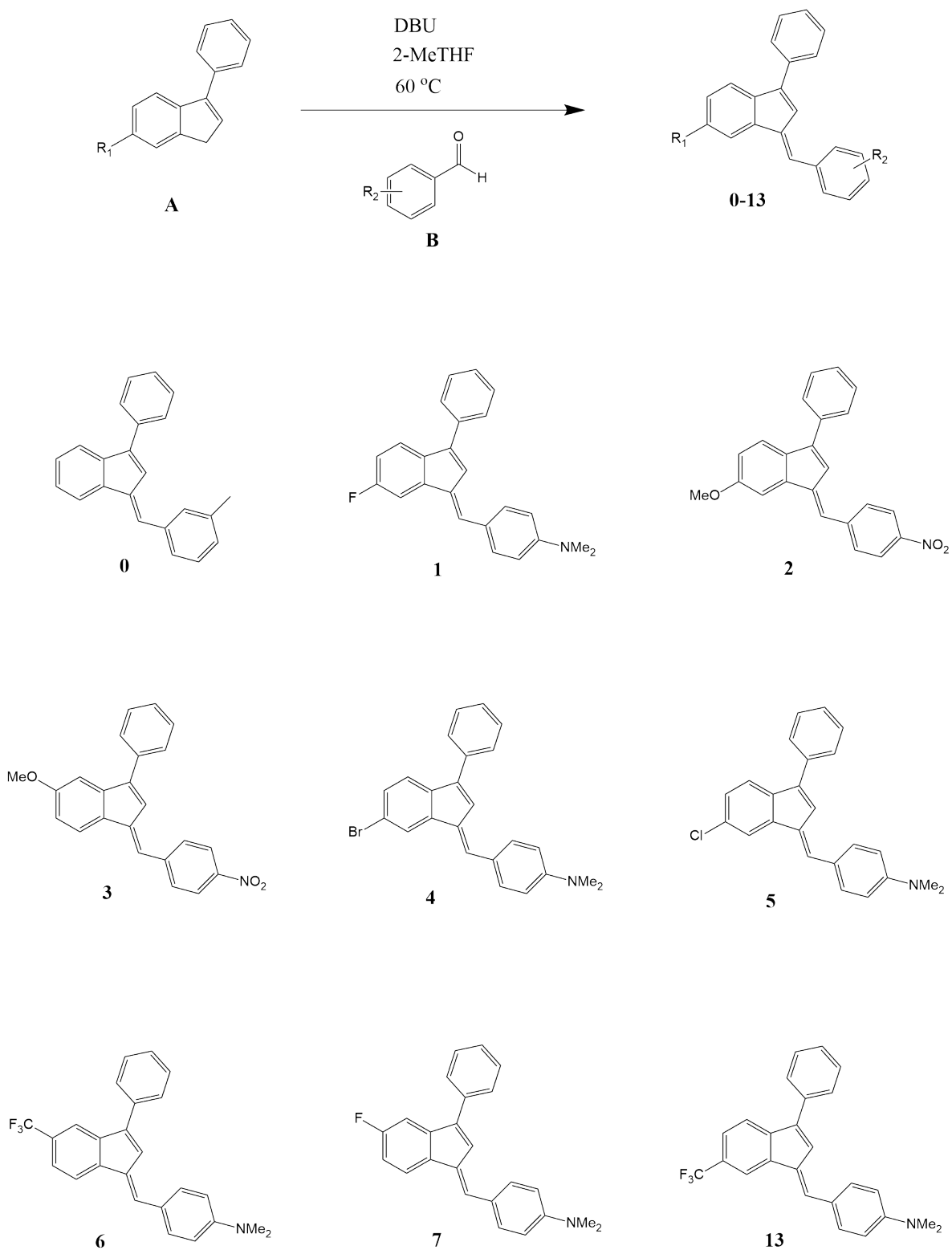


previous two steps are repeated twice more before the addition of a previously decided amount of indanone. The RBF is exposed to vacuum for 5 minutes and N<sub>2</sub> gas once more, before an excess of 2-MeTHF is inserted through a needle. The flask is stirred and cooled to 0 °C before a 3 M solution of PhMgBr in 2-MeTHF are added dropwise. After waiting for 30 minutes, diethyl phosphite is added dropwise to the RBF and stirred overnight.

Ammonium chloride and ethyl acetate are added to separate the solution into aqueous and organic layers. The aqueous layer at the bottom is removed, and MgSO<sub>4</sub> is mixed into the remaining organic portion until dry. Then, the contents of the RBF are gravity filtered and remaining solvents are removed under reduced pressure. The indene product is isolated using column chromatography and characterized with TLC. Most of the solvent is then removed under reduced pressure, but enough is left that the indene product is dissolved and can be transferred into a tared RBF or scintillation vial. Then, the remaining solvent is removed and the indene is stored in a freezer until needed for benzofulvene synthesis.

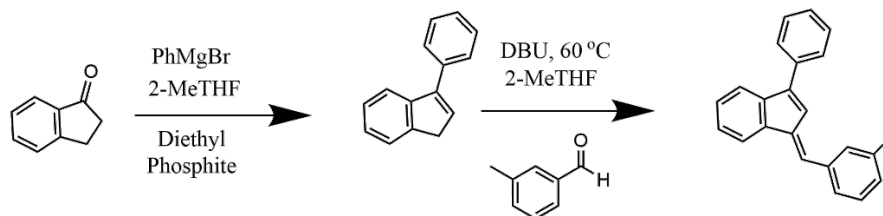
### **General Synthesis of Benzofulvene Monomers**

The following reactants are added to the RBF containing indene: an excess of 2-MeTHF, a functionalized benzaldehyde, and DBU. The solution is exposed to stirring and a temperature of 60 °C for approximately 10 minutes. Before proceeding, TLC is ran to confirm the presence of benzofulvene with minimal impurities. Then, solvents are removed under reduced pressure. Afterwards, the benzofulvene product is isolated using column chromatography with dry-loading (also with a 90:10 hexanes:EtOAc eluent), and characterized with TLC and proton NMR.



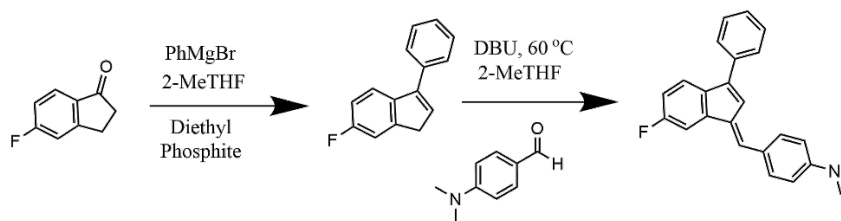
**Scheme 1.** General reaction scheme and substrate scope for benzofulvene synthesis via the heated addition of benzaldehydes to indenes.

## Synthesis of Benzofulvenes 0-13



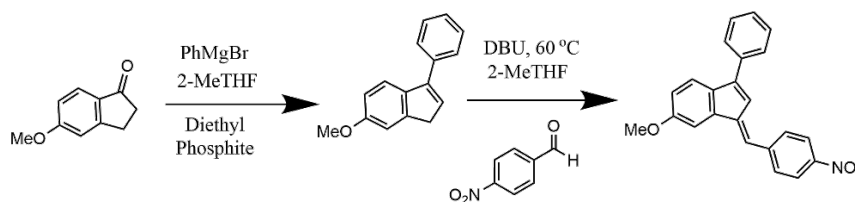
**Scheme 2.** Synthesis of 0.

1-indanone (300 mg, 2.27 mmol) and 2-MeTHF (3.1 mL) were added to a dry, N<sub>2</sub>-flushed RBF. Stirring was applied and the solution was cooled to 0 °C. Phenylmagnesium bromide (0.45 mL, 2.50 mmol, 3 M solution in 2-MeTHF) was then added dropwise. After 30 minutes, diethyl phosphite (0.63 mL, 4.54 mmol) was added, and the reaction was left to stir overnight. The next day, ethyl acetate (5 mL) and NH<sub>4</sub>Cl (5 mL) were added to the RBF. The aqueous layer was removed and the organic layer was dried using anhydrous MgSO<sub>4</sub>, after which the solvent was removed under reduced pressure. The resulting crude oil was purified via column chromatography (90:10 Hex:EtOAc). 92 mg (0.48 mmol) of phenyl indene was collected in an RBF for benzofulvene synthesis, where it was combined with 2-MeTHF (~1 mL), 3-methylbenzaldehyde (0.06 mL, 0.53 mmol) and DBU (0.08 mL, 0.53 mmol). Stirring was applied, the RBF was configured with an air condenser, and the reaction was left at 60 °C for 10 minutes. The solvent was removed under reduced pressure, and the crude oil underwent column chromatography (90:10 Hex:EtOAc).



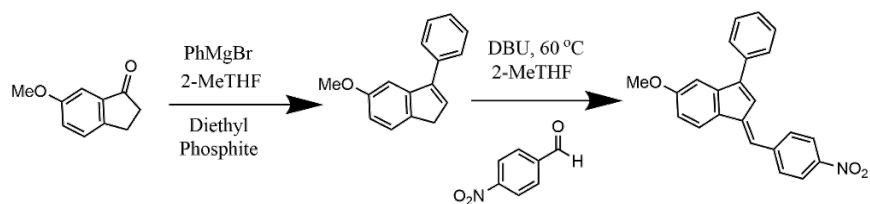
**Scheme 3.** Synthesis of **1**.

The procedure for **0** was followed with 5-fluoro-1-indanone (381 mg, 2.53 mmol), 2-MeTHF (3.3 mL), phenylmagnesium bromide (0.88 mL, 2.64 mmol, 3 M solution in 2-MeTHF), and after a 34-minute wait, diethyl phosphite (0.67 mL, 5.17 mmol) for the indene precursor synthesis, and the resulting phenyl indene (285 mg, 1.36 mmol), 2-MeTHF (3 mL), 4-dimethylaminobenzaldehyde (228 mg, 1.53 mmol), and DBU (0.22 mL, 1.49 mmol) for the benzofulvene synthesis.



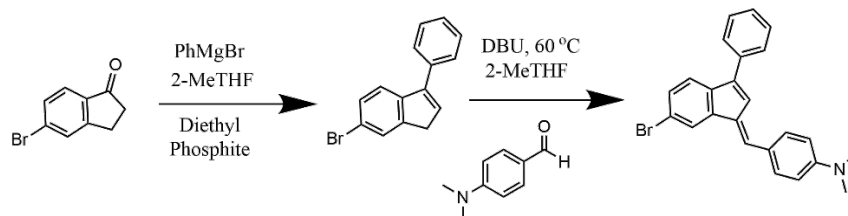
**Scheme 4.** Synthesis of **2**.

The procedure for **0** was followed with 5-methoxy-1-indanone (400 mg, 2.47 mmol), 2-MeTHF (5.11 mL), phenylmagnesium bromide (1.23 mL, 3.70 mmol, 3 M solution in 2-MeTHF), and after a 60-minute wait, diethyl phosphite (0.57 mL, 4.44 mmol) for the indene precursor synthesis, and the resulting phenyl indene (209 mg, 0.94 mmol), 2-MeTHF (2.19 mL), 4-nitrobenzaldehyde (142 mg, 0.94 mmol), and DBU (0.14 mL, 0.94 mmol) for the benzofulvene synthesis. This solution was heated at 60 °C for 8 minutes in a septum vial with a needle. An eluent of 70:30 hexanes:EtOAc was used for the benzofulvene.



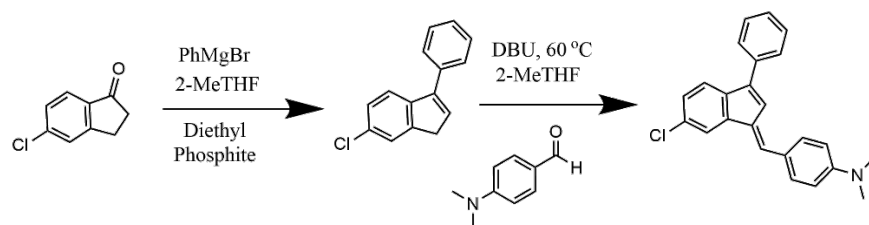
**Scheme 5.** Synthesis of **3**.

The procedure for **0** was followed with 6-methoxy-1-indanone (202 mg, 1.25 mmol), 2-MeTHF (2.50 mL), phenylmagnesium bromide (0.56 mL, 1.68 mmol, 3 M solution in 2-MeTHF), and after a 30-minute wait, diethyl phosphite (0.61 mL, 4.74 mmol) for the indene precursor synthesis, and the resulting phenyl indene (83 mg, 0.57 mmol), 2-MeTHF (1.53 mL), 4-nitrobenzaldehyde (94 mg, 0.63 mmol), and DBU (0.170 mL, 1.14 mmol) for the benzofulvene synthesis.



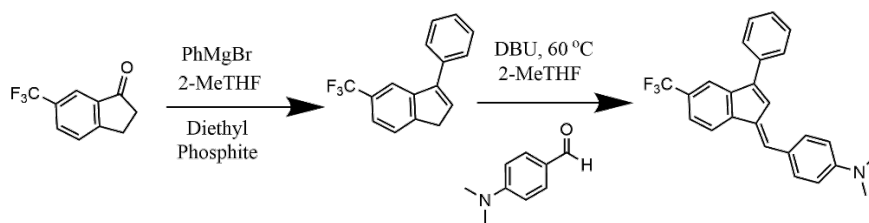
**Scheme 6.** Synthesis of **4**.

The procedure for **0** was followed with 5-bromo-1-indanone (200 mg, 0.95 mmol), 2-MeTHF (1.59 mL), phenylmagnesium bromide (0.47 mL, 1.42 mmol, 3 M solution in 2-MeTHF), and after a 28-minute wait, diethyl phosphite (0.21 mL, 1.66 mmol) for the indene precursor synthesis, and 100 mg of the resulting phenyl indene (0.37 mmol), 2-MeTHF (1 mL), 4-dimethylaminobenzaldehyde (55 mg, 0.37 mmol), and DBU (0.055 mL, 0.37 mmol) for the benzofulvene synthesis.



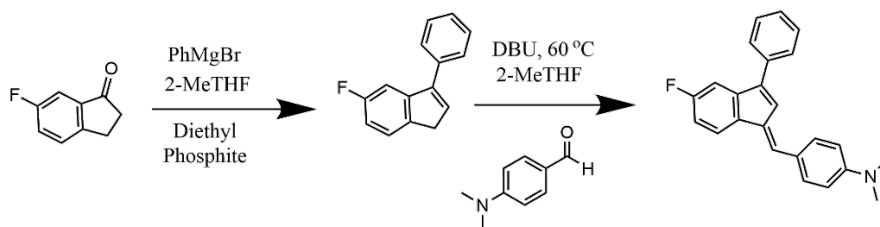
**Scheme 7.** Synthesis of **5**.

The procedure for **0** was followed with 5-chloro-1-indanone (200 mg, 1.2 mmol), 2-MeTHF (2.02 mL), phenylmagnesium bromide (0.60 mL, 1.80 mmol, 3 M solution in 2-MeTHF), and after a 37-minute wait, diethyl phosphite (0.28 mL, 2.16 mmol) for the indene precursor synthesis, and 104 mg of the resulting phenyl indene (0.46 mmol), 2-MeTHF (1 mL), 4-dimethylaminobenzaldehyde (69 mg, 0.46 mmol), and DBU (0.069 mL, 0.46 mmol) for the benzofulvene synthesis.



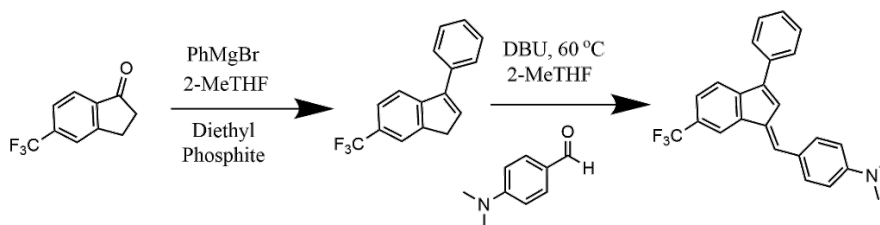
**Scheme 8.** Synthesis of **6**.

The procedure for **0** was followed with 6-trifluoromethyl-1-indanone (100mg, 0.50 mmol), 2-MeTHF (1 mL), and phenylmagnesium bromide (0.33 mL, 1 mmol, 3 M solution in 2-MeTHF). 25 minutes into the reaction, it was realized that solvent had evaporated - 2-MeTHF (1.5 mL) was readded, positive N<sub>2</sub> pressure was reestablished, and reaction was allowed to continue. Then, diethyl phosphite (0.14 mL, 1.09 mmol) was added to finish the indene precursor synthesis. 52 mg of the resulting phenyl indene (0.20 mmol), 2-MeTHF (1 mL), 4-dimethylaminobenzaldehyde (33 mg, 0.22 mmol), and DBU (0.033 mL, 0.22 mmol) were used for the benzofulvene synthesis.



**Scheme 9.** Synthesis of **7**.

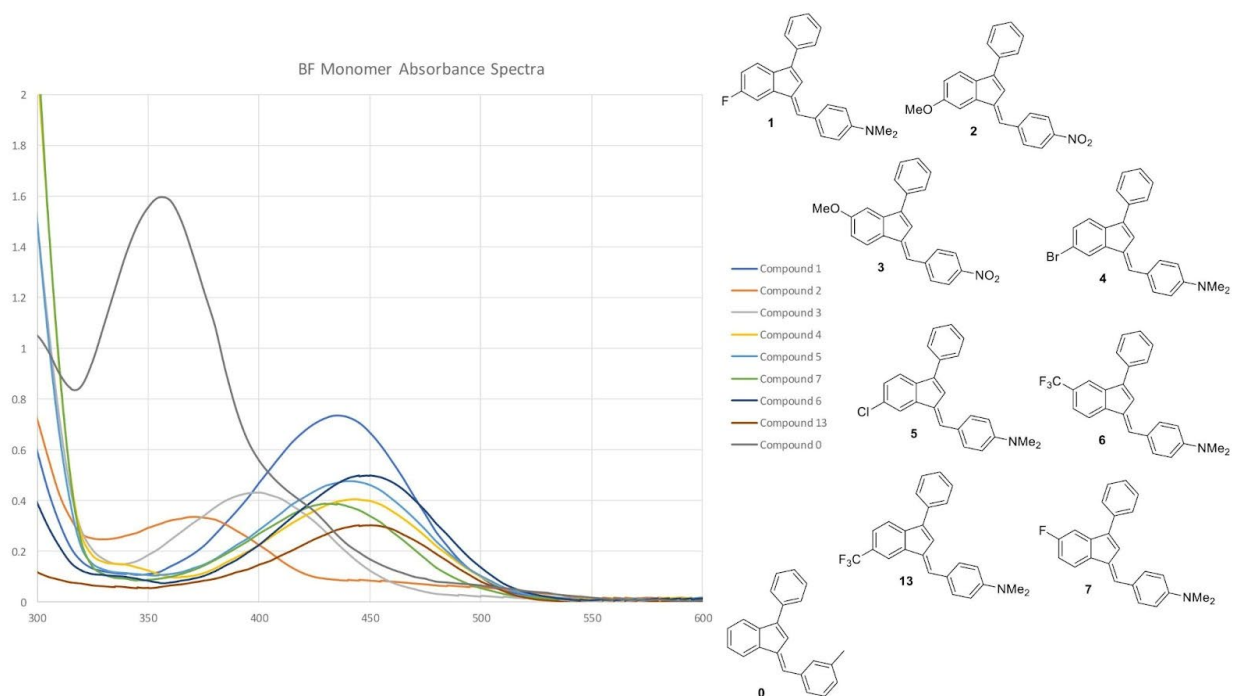
The procedure for **0** was followed with 6-fluoro-1-indanone (300 mg, 2.0 mmol), 2-MeTHF (3.36 mL), phenylmagnesium bromide (1.0 mL, 3.0 mmol, 3 M solution in 2-MeTHF), and after a 35-minute wait, diethyl phosphite (0.46 mL, 3.6 mmol) for the indene precursor synthesis, and 100 mg of the resulting phenyl indene (0.48 mmol), 2-MeTHF (1.29 mL), 4-dimethylaminobenzaldehyde (75 mg, 0.50 mmol), and DBU (0.091 mL, 0.60 mmol) for the benzofulvene synthesis. An aqueous layer was separated and removed after heating the benzofulvene reaction.



**Scheme 10.** Synthesis of **13**.

The procedure for **0** was followed with 5-trifluoromethyl-1-indanone (200 mg, 1.0 mmol), 2-MeTHF (2 mL), phenylmagnesium bromide (0.36 mL, 1.1 mmol, 3 M solution in 2-MeTHF), and after a 30-minute wait, diethyl phosphite (0.28 mL, 2.1 mmol) for the indene precursor synthesis, and 136 mg of the resulting phenyl indene (0.53 mmol), 2-MeTHF (2 mL), 4-dimethylaminobenzaldehyde (87 mg, 0.58 mmol), and DBU (0.087 mL, 0.58 mmol) for the benzofulvene synthesis. The benzofulvene reaction was heated to 90 °C for 30 minutes.

## Results and Discussion



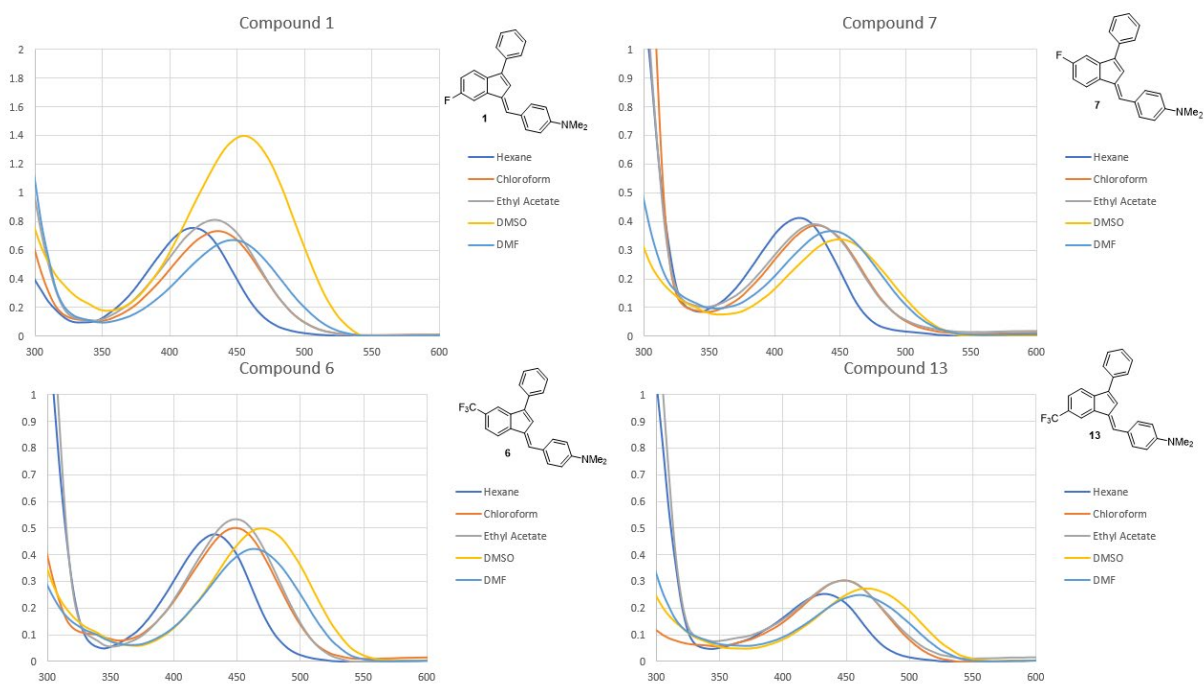
**Figure 10.** UV-vis absorbance spectra for all benzofulvene monomers, where the horizontal axis represents photon wavelength in nm.

Thus far, we have succeeded in creating some optical tunability in the visible light range. However, these monomers primarily appear red or orange, given their absorbance of blue wavelengths seen in Figure 10. Future research should explore a wider range of accessible, strongly electron-donating or withdrawing substituents as well as modified benzofulvene structures conducive to conjugation.

Red-shifting (denoted by higher  $\lambda_{\max}$  values) is most prominent in the  $\text{CF}_3$ -substituted benzofulvenes **6** and **13**, which makes sense as  $\text{CF}_3$  is an incredibly strong EWG. The parent compound **0**, as well as compounds **2** and **3** where the locations of the EDG and EWG on the benzofulvene are swapped, experience considerable blue-shifting. In addition, monomers **1** and **13** experience a greater degree of red-shifting than their EWG-equivalent counterparts **7** and **6**,



respectively. This suggests that a stronger delocalization effect results from having an EWG on the ‘lower’ 6- position than on the ‘upper’ 5- position.

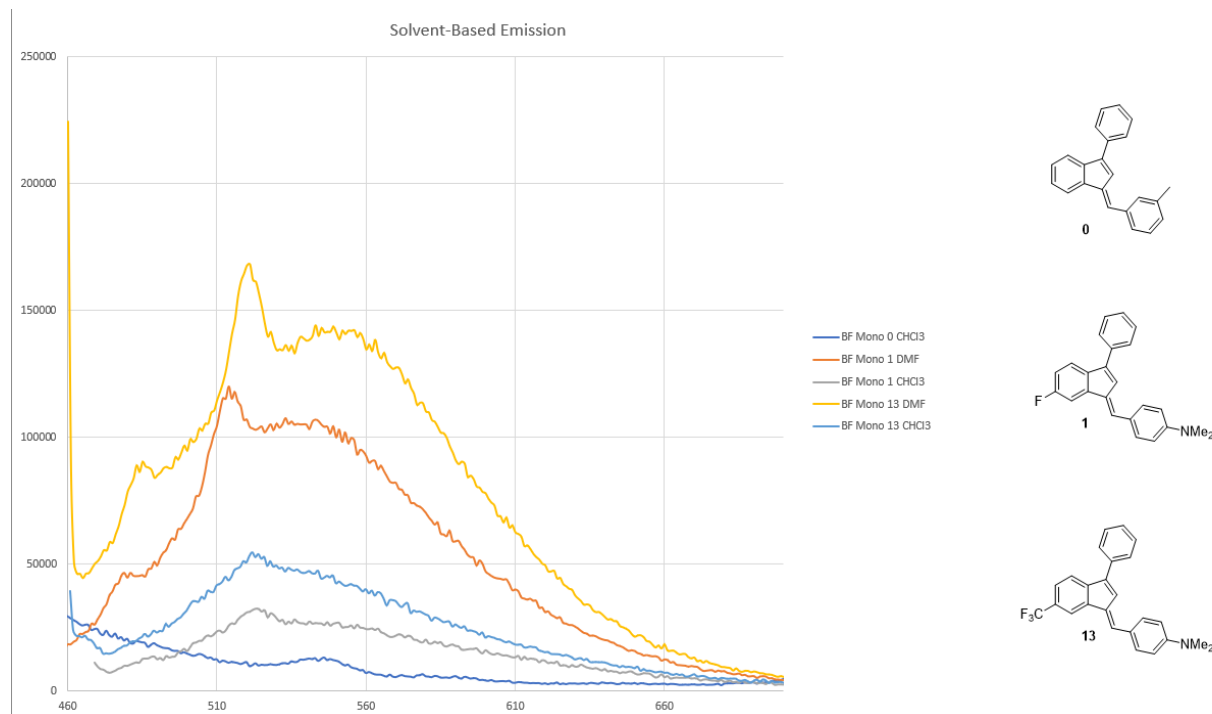


**Figure 11.** Absorbance spectra for 1, 6, 7, and 13 in various solvents.

Figure 11 shows that different solvents induce changes in the  $\lambda_{max}$  of the selected compounds (thereby red-shifting or blue-shifting the monomers) in a phenomenon known as solvatochromism. Solvent polarity is shown to influence absorption wavelengths. Functionalized benzofulvenes with one end donating electrons and another end withdrawing them are polar molecules with zwitterionic properties. Polar viscous solvents such as DMF can stabilize the zwitterionic charge, increasing solubility and red-shifting. In nonpolar solvents like hexanes, these monomers may have reduced solubility and systemic conjugation, resulting in the blue-shifting seen with hexane in Figure 11.

Solvatochromism can be used to one’s advantage when designing an optically tunable system. The variability in absorbance wavelengths due to modifiable substituent groups as

shown in Figure 10 can be enhanced by the use of interchangeable solvents, leading to an overall wider range of colors.

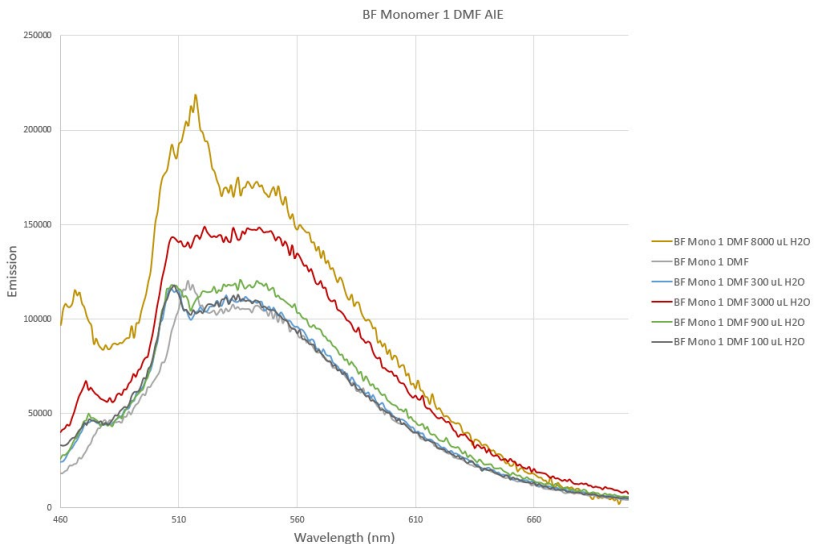


**Figure 12.** Emission spectra for **1** and **13** in CHCl<sub>3</sub> and DMF with the parent compound **0** in CHCl<sub>3</sub> as a control.

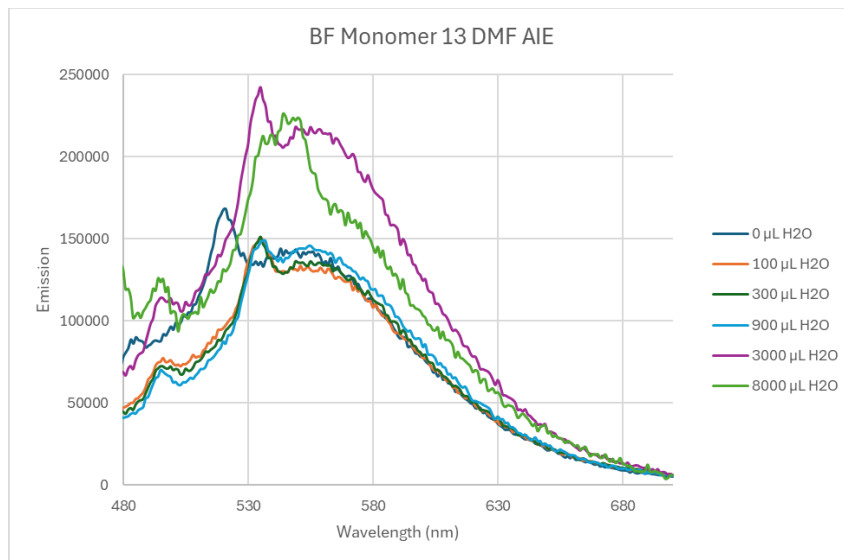
As seen in Figure 12, DMF increases the emission intensity of benzofulvenes **1** and **13**. Viscous solvents like DMF restrict exocyclic bond rotation, improving the planarity and systemic conjugation of benzofulvenes. Figures 11 and 12 highlight a potential correlation between solvent-based red-shifting and fluorescence.

This poses a conundrum: it may be difficult for an optoelectronic designer to achieve a solvent-based increase in absorbance wavelength or emission intensity in isolation. Future research could investigate absorbance and emission spectra using a wider range of solvents to compare the extents to which polarity, viscosity, and other characteristics affect the optical properties of benzofulvenes. In addition, absorbance spectra of colloidal nanoparticle solutions

can be tested to determine unique optical changes that complement solvent variability (and a possible solution to the aforementioned conundrum).



**Figure 13.** AIE spectra for **1** in DMF and varying levels of H<sub>2</sub>O. Corrections were made accounting for changes in benzofulvene concentration from H<sub>2</sub>O addition.



**Figure 14.** AIE spectra for **13** in DMF and varying levels of H<sub>2</sub>O, with corrections.

The AIE spectra presented in Figures 13 and 14 highlight a nonlinear relationship between the amount of water used to dilute benzofulvenes in DMF and emission intensity. This is especially clear in Figure 14, where solutions diluted with 3000  $\mu$ L and 8000  $\mu$ L of water have somewhat

equally-strong increases in fluorescence. Figure 13 also shows relatively weak AIE effects until the 3000  $\mu\text{L}$  dilution. These results suggest that a specific degree of dilution is required for the formation of a colloid where bond rotation is restricted and fluorescence is optimized.

It should be noted that the emission data in Figures 13 and 14 has been corrected to equilibrate benzofulvene concentrations in variably-diluted samples. In practice, highly dilute solutions still fluoresce less intensely than the respective monomers in DMF alone, but AIE promotes efficiency in practical applications – less benzofulvene needs to be produced in order to achieve similar emission intensities.

## Conclusion

To conclude, a range of tunable benzofulvene monomers with electron push-pull conjugation systems were synthesized using a mild, straightforward route developed by Glass et al. in previous research.<sup>21</sup> Optical properties were found to be influenced by variable electron-donating and withdrawing substituents, solvents, and aggregation. Specifically, the greatest degree of red-shifting can be achieved using a monomer with a strong EWG on the 6- position of the indene moiety dissolved in a polar viscous solvent. Current limitations that can be addressed in future research include unrecorded yields, an incomplete visible light spectrum, and difficulty isolating absorbance and emission tunabilities.

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