

Article

The Preparation and Photophysical Properties of 3-Substituted 4-Azafluorenones

Amanda K. Stebner , Christopher J. Abelt *  and Jonathan R. Scheerer * 

Department of Chemistry, College of William and Mary, Williamsburg, VA 23185, USA; akstebner@wm.edu

* Correspondence: cjabel@wm.edu (C.J.A.); jrscheerer@wm.edu (J.R.S.)

Abstract

A method for the preparation of 3-substituted azafluorenones is presented. Condensation of ninhydrin with thiomethylamidrazone gives a triazine from which 3-thiomethyl-4-azafluorenone is produced after Diels–Alder cycloaddition with norbornadiene followed by two retro-Diels–Alder cycloreversions. Oxidation of the sulfide to the sulfone allows for nucleophilic substitution at the 3-position. Using different amidrazones can give other substituents at the 3-position directly. The photophysical properties of the azafluorenones are characterized and compared with computational calculations. Compounds with a substituent bearing an n-donor group show significant fluorescence. The n-donor group is prominent in the HOMOs in these systems, whereas in the compounds with weak emission, it is not. The El Sayed rules for intersystem crossing do not explain the emission intensity ordering of these compounds.

Keywords: 4-azafluorenone; fluorescence; triazine

1. Introduction

Fluorenone (Figure 1) is a simple diaryl ketone whose photochemical properties have been the subject of numerous studies over many years. Like benzophenone, it undergoes facile intersystem crossing in nonpolar solvents and can function as a triplet sensitizer [1], sometimes giving better outcomes compared to other sensitizers [2,3]. The fundamental photophysical properties of fluorenone [4,5] continue to be refined [6–8]. As the understanding of fluorenone has improved, so have its applications been enabled in a variety of areas [9], including resistive memory devices [10], thermally activated delayed fluorescent materials [11], and photoredox catalysis [12].

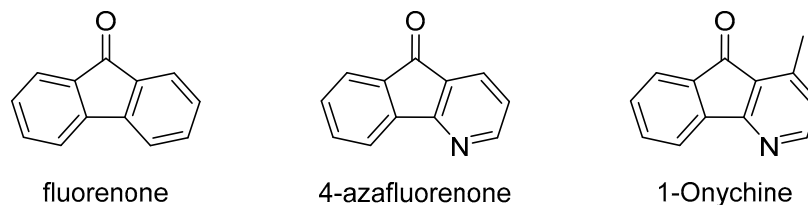


Figure 1. Structures of fluorenone, 4-azafluorenone, and 1-Onychine.

The photophysical properties of fluorenone are strongly affected by some substituents. Amines in the 3-position allow for direct resonance with the carbonyl group, and these compounds give rise to stronger fluorescence and solvatofluorochromism from the intramolecular charge transfer (ICT) excited states [13–15]. The fluorescence is strongly



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quenched in alcohol solvents. The more electron-rich carbonyl oxygen forms H-bonds with the alcohol solvent in the excited state. The geometry and stoichiometry of the excited-state H-bonding interactions have been investigated, and different interpretations have been put forward to explain the quenching behavior [16].

Replacing one or both benzene rings with pyridine or other azaaromatics results in a different core skeleton that may have different photophysical properties. This paper focuses exclusively on 4-azafluorenones derivatives (Figure 1). A number of these have been reported in the natural products literature. Onychine [17], bearing a methyl group in the 1-position (Figure 1), is the simplest member of this group, but many other 4-azafluorenone natural products bearing different substituents are also known [18–20].

Because fluorenones have been shown to have useful medicinal and photochemical applications, we were interested in exploring this chemical space further. Our recent work showed that 4-azafluorenones could be prepared relatively rapidly from commercially available amidrazones. We wanted to develop a method where a variety of 4-azafluorenones could be prepared from a common, inexpensive amidrazone. In this paper, we report a general route for the preparation of 3-substituted 4-azafluorenones. The compounds prepared in this study are shown in Figure 2. The photophysical properties, especially their fluorescence and solvatofluorochromism, are reported with a focus on characterizing how the substituents affect these properties.

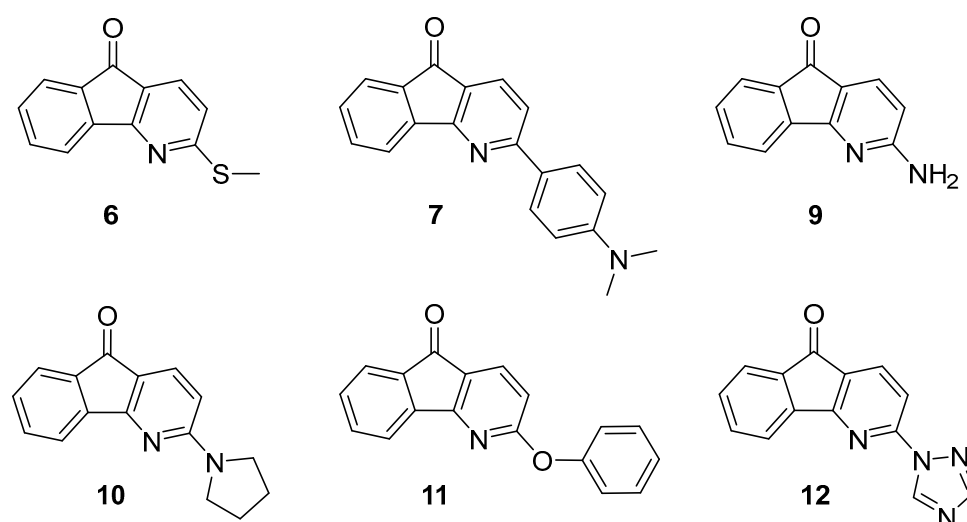


Figure 2. Structures of 4-azafluorenone compounds prepared in this study.

2. Results

2.1. Synthetic Approaches

2.1.1. General Pericyclic Cascade

The general route to 3-substituted 4-azafluorenones (Figure 3) follows our preparation of Onychine [21]. Condensation of amidrazone (2) with ninhydrin (1) gives a triazine (4); complementary reaction with amidrazone 3 gives triazine 5. Diels–Alder reaction of the triazine function with norbornadiene, a non-nucleophilic alkyne-equivalent 2π reaction component, affords the azafluorenones after the sequential extrusion of N_2 and cyclopentadiene. These three pericyclic reactions are done in a single vessel. The structure of the amidrazone determines whether the substituent at the 3-position can be elaborated further.

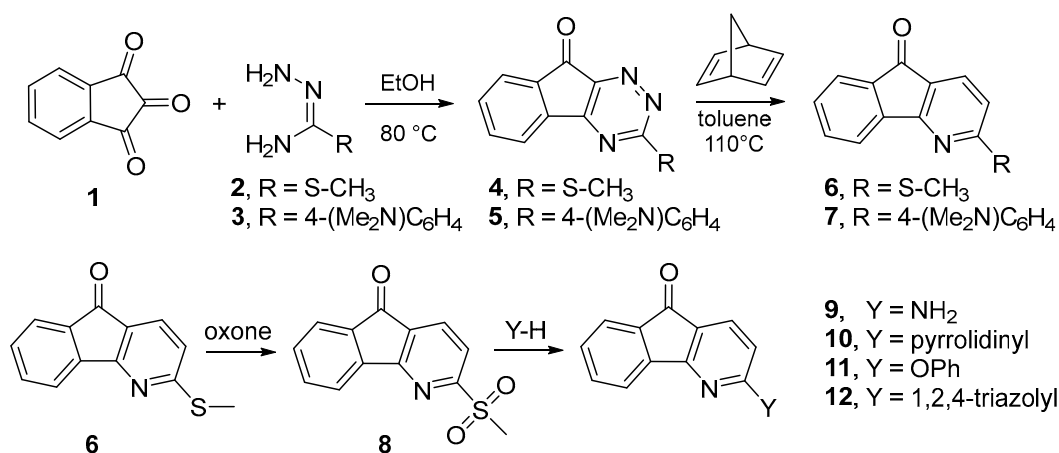


Figure 3. Synthetic routes to various 3-substituted 4-azafluorenones.

2.1.2. Route from Thiomethylamidrazone **2**

For the majority of the azafluorenones derivatives, we wanted to find a common amidrazone precursor that could be elaborated into a variety of targets. While the thiomethyl amidrazone is commercially available, it is also conveniently made by methylation of thiosemicarbazide [22]. The thiomethyl triazine undergoes facile reaction with norbornadiene to give 3-thiomethyl-4-azafluorenone (**6**). The substituent so positioned is a vinylogous thioester and may be capable of undergoing nucleophilic substitution. Direct S_NAr displacement of the thiomethyl functionality was not ideal. We reasoned that transforming the thiomethyl group into a better leaving group would be more efficacious. Oxidation of the thiomethyl group with oxone gave mostly the sulfone with a persistent but very small amount of the sulfoxide. Both sulfur groups are better leaving groups than the sulfide. We were able to conduct nucleophilic substitution on this mixture without separating these oxides.

2.1.3. Route from Dimethylaminophenylamidrazone **3**

The 3-substituent can be incorporated directly into the amidrazone. This process requires preparing the Pinner salt **14** from the corresponding nitrile **13** and anhydrous HCl in methanol (Figure 4). Neutralization of the Pinner salt followed by displacement of the methoxy group with hydrazine gives the amidrazone. From this point, the sequence is the same: reaction with ninhydrin, followed by cycloaddition with norbornadiene and sequential cycloreversions.

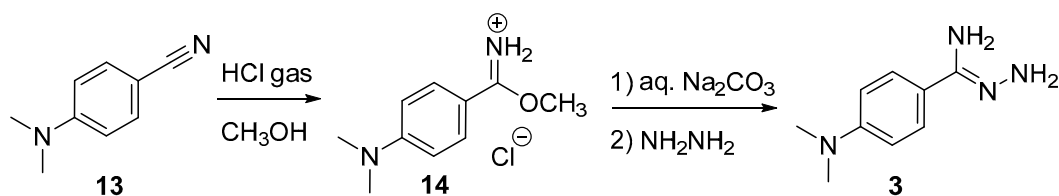


Figure 4. Preparation of amidrazone **3** from Pinner salt **14**.

2.2. Photophysical Studies

2.2.1. Absorption

In addition to the strong absorption below 300 nm due to the aromatic moieties, these compounds all show an absorption band between 300 and 400 nm (Figure 5). The three with a nitrogen atom donor group (**7**, **9–10**) also show a long-wavelength band greater than 400 nm (Table 1). For these compounds, the intermediate absorption bands between 300 and 400 nm have high molar absorptivities ($\log \epsilon > 4$), and the additional long-wavelength

band decreases in molar absorptivity in the order $7 > 10 > 9$. The long-wavelength band is red-shifted in ethanol. For comparison, this band is blue-shifted in 3-aminofluorenones [16]. While the sulfur donor compound **6** shows a strong intermediate absorption band, the triazole (**12**) and oxygen donor (**11**) compounds do not. Note that the lone pair of the attached nitrogen of the triazole is part of the aromatic system of the triazole and is not by itself a donor group. By way of comparison, the related 3-thiomethylfluorenone shows a $\lambda_{\max}$ at 450 nm ($\log \epsilon = 2.84$) [23]. 3-Phenyl-4-azafluorenone shows a $\lambda_{\max}$ at 376 nm [24] in THF.

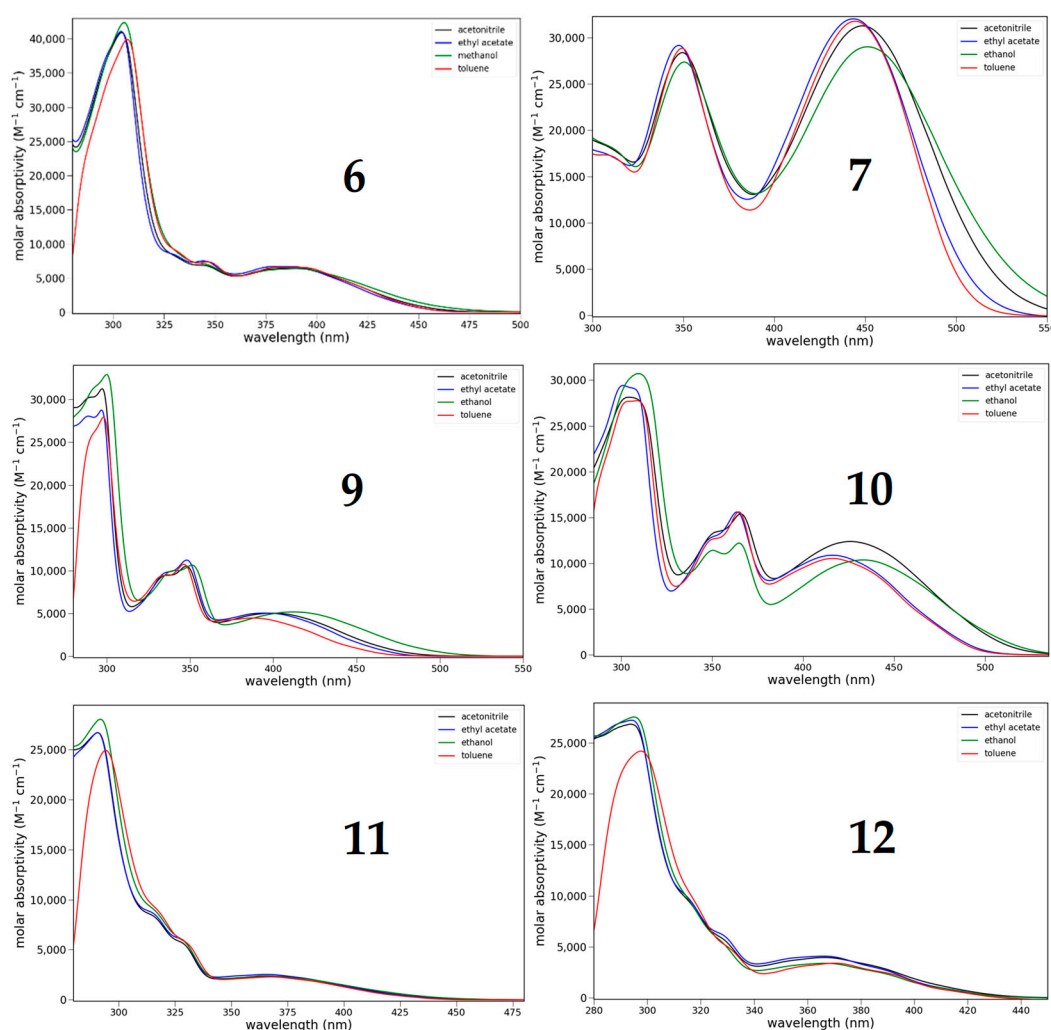


Figure 5. UV-VIS spectra calculated for **6**, **7**, **9–12** in acetonitrile (—), ethyl acetate (—), ethanol (—), and toluene (—) using the method of standard additions.

Table 1. Long-wavelength absorption maxima for **6**, **7**, **9–12** in toluene.

	6	7	9	10	11	12
$\lambda_{\max}$ (nm)	391	445	387	417	367	370
$\log \epsilon$	3.82	4.50	3.64	4.02	3.39	3.53

2.2.2. Fluorescence

The fluorescence of compounds **6**, **7**, **9–12** shows a range of behaviors (Figure 6 and Table 2). The fluorescence efficiencies vary between a maximum of 88% for **7** in toluene to a minimum of 0.02% for **12** in cyclohexane. The relative fluorescence intensities were determined through relative quantum yield determinations using anthracene as a reference

($\Phi = 0.30$) and toluene as the solvent. The quantum yields for **6**, **7**, **9–12** are 0.137 ± 0.015 , 0.877 ± 0.035 , 0.059 ± 0.002 , 0.099 ± 0.008 , 0.0023 ± 0.0003 , and 0.0005 ± 0.0002 , respectively. The maximum emission efficiencies for the three with a nitrogen atom donor (**7**, **9–10**) follow the same order as their molar absorptivities: **7** (88%, toluene) > **10** (23%, cyclohexane) > **9** (6%, toluene). Compound **6**, bearing a sulfur atom donor group, was surprisingly fluorescent. Not only is its molar absorptivity relatively small ($\log \epsilon < 4$), but because sulfur is a heavy atom, it should also contribute to spin-orbit-coupling-enhanced deactivation [4]. Nevertheless, its fluorescence efficiency is 33% in acetonitrile. Both the phenol **11** and triazole **12** derivatives were weakly fluorescent, topping out at 0.5% in acetonitrile and isopropanol, respectively. The nitrogen atom donors (**7**, **9–10**) fluoresce most strongly in apolar solvents, while **6** fluoresces most strongly in polar, aprotic solvents. Protic solvents quench the emission of **7**, **9–10**. The quenching is weaker with **6** but is still evident.

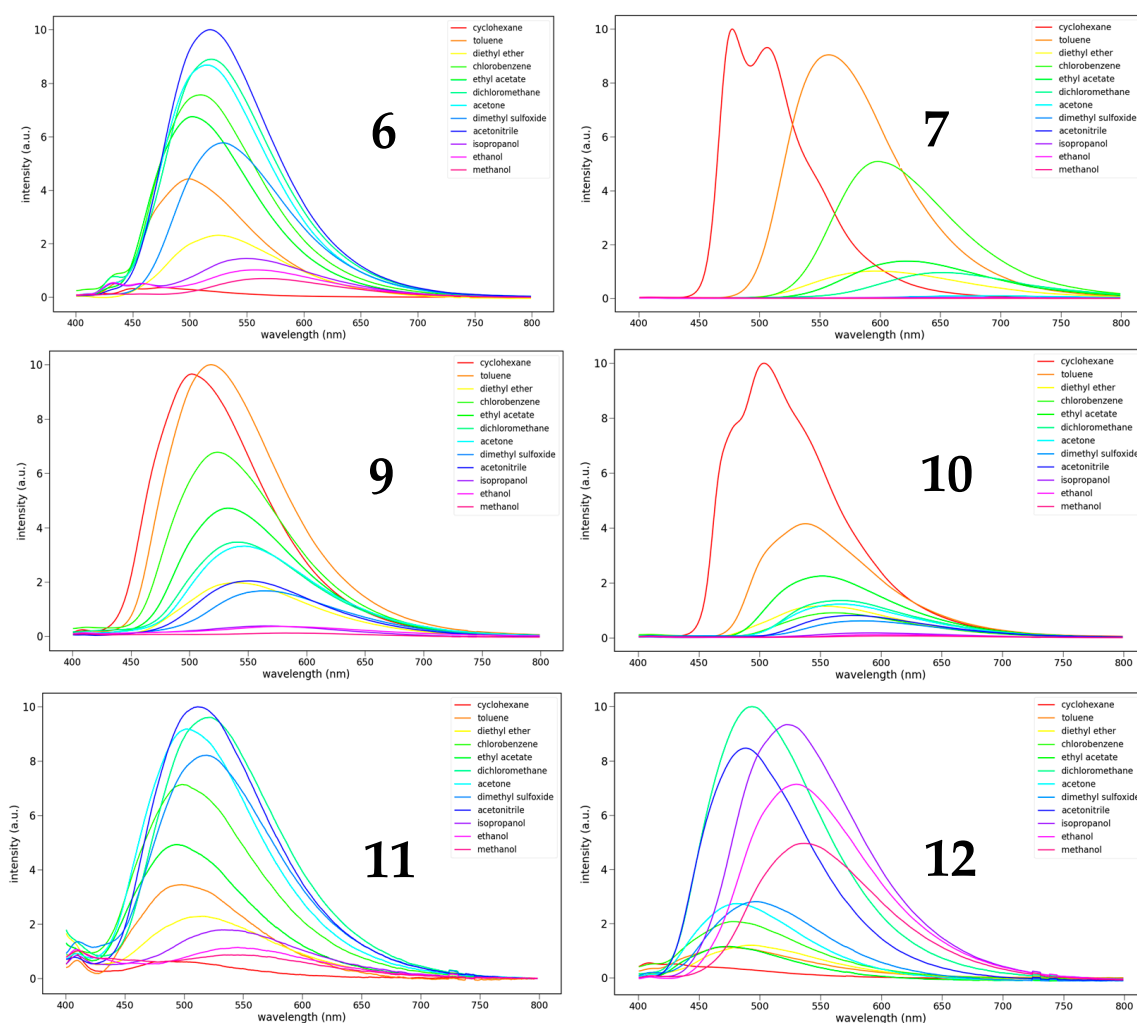


Figure 6. Fluorescence spectra of 2.4×10^{-5} M **6**; 4.6×10^{-6} M **7**; 6.2×10^{-5} M **9**; 8.2×10^{-6} M **10**; 2.0×10^{-5} M **11**; 1.1×10^{-5} M **12** in cyclohexane (—), toluene (—), diethyl ether (—), chlorobenzene (—), ethyl acetate (—), dichloromethane (—), acetone (—), dimethylsulfoxide (—), acetonitrile (—), isopropanol (—), ethanol (—), and methanol (—). Excitation at 366 nm.

Table 2. Emission maxima (nm) and relative quantum yields (Φ) for **6**, **7**, **9–12** in various solvents.

Solvent	6		7		9		10		11		12	
	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$	$\lambda_{\max}$ (nm)	Φ $\times 10^{-3}$
(CH ₂) ₆	478	11	509	717	513	54	518	226	505	0.3	434	0.2
PhMe	504	137	566	877	528	59	544	99	493	2.3	491	0.5
Et ₂ O	531	108	611	133	552	13	562	31	520	1.3	499	0.7
PhCl	517	244	607	541	531	41	570	25	515	3.6	492	1.0
EtOAc	511	210	634	172	541	30	560	57	501	2.4	480	0.7
CH ₂ Cl ₂	527	297	662	126	552	22	576	36	528	4.9	501	4.5
Me ₂ CO	523	285	701	17	557	22	575	33	515	4.5	490	1.4
DMSO	536	193	741	7	575	12	595	19	527	4.3	505	1.5
MeCN	526	326	736	5	560	14	586	22	522	5.0	494	3.8
<i>i</i> PrOH	560	64	673	10	576	3	602	6	549	1.2	532	4.8
EtOH	571	50	697	5	598	3	618	4	558	0.9	538	3.8
MeOH	576	33	435	5	607	1	634	3	559	0.8	548	2.8

2.2.3. Solvatofluorochromism

All derivatives showed solvatofluorochromism. Evidence for this behavior is shown in Figure 7. In this graph, the center-of-gravity emission in wavenumbers is plotted vs. the Reichardt solvent polarity parameter ($E_T(30)$). The best-fit lines all show negative slopes, indicating that the emission shifts to lower wavenumbers (higher wavelengths) as the solvent polarity increases. This phenomenon indicates that the excited state is more polar than the ground state and suggests some intramolecular charge transfer. Polar solvents better stabilize the excited state and lead to lower-energy fluorescence. The magnitude of the solvatofluorochromism is quantified by the slopes of the best-fit lines (Table 3). The solvatofluorochromism is not dramatic except for compound **7**, whose slope is 3.5 to 7.8 times greater than the rest. Note that some of the lines do not extend completely to $E_T(30) = 55.4$ (CH₃OH). Points were excluded when the quenching was so strong that the determination of the emission center of gravity was not reliable.

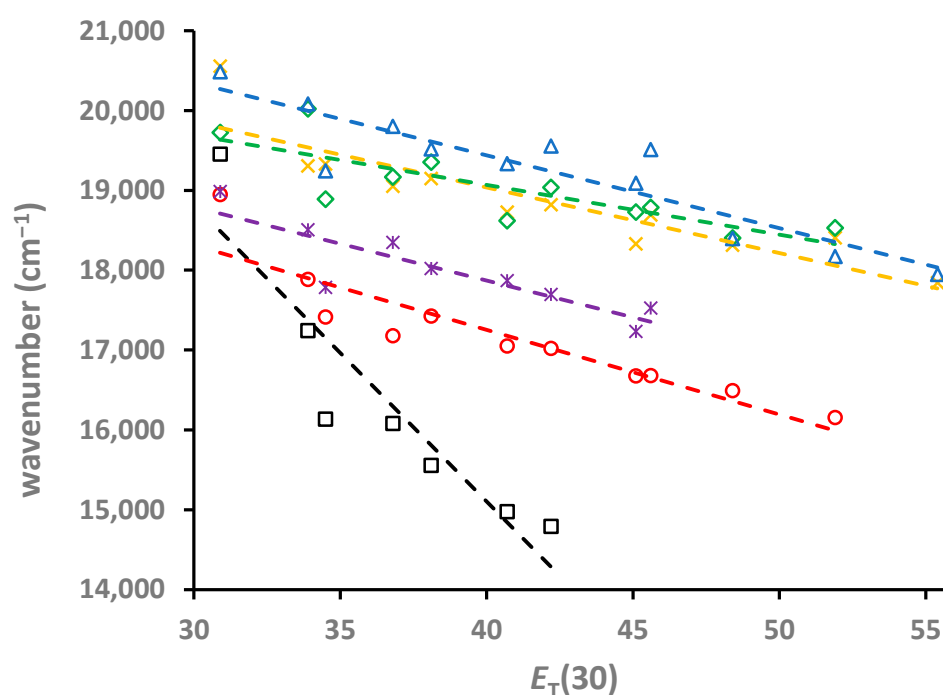


Figure 7. Solvatofluorochromism plots of center-of-gravity emission maxima (cm^{−1}) vs. $E_T(30)$ for **6** (x, orange), **7** (□, black), **9** (*, purple), **10** (o, red), **11** (Δ, blue), and **12** (◇, green).

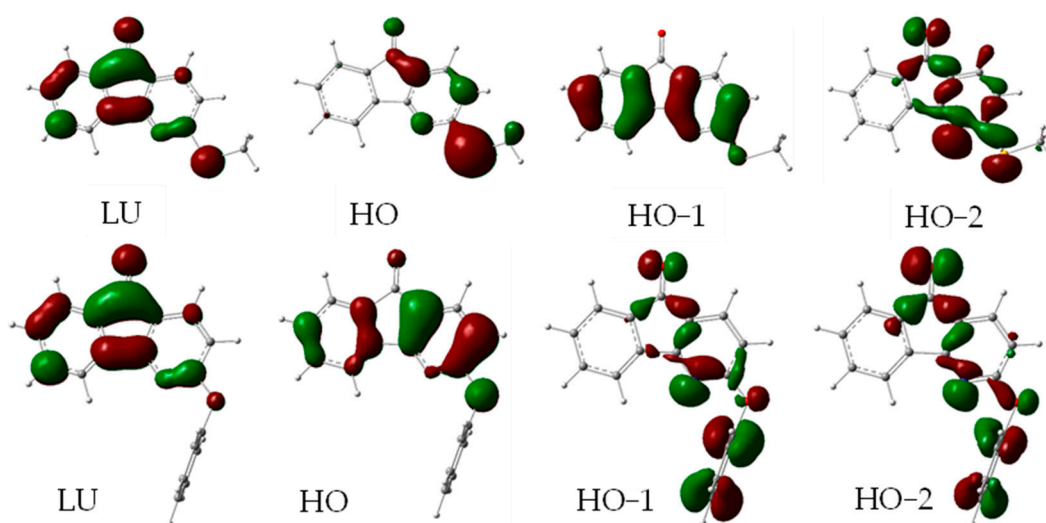
Table 3. The slopes of the best-fit lines for the solvatofluorochromism plots of **6**, **7**, **9–12**.

	6	7	9	10	11	12
Slope	−82	−373	−92	−106	−48	−88
R^2	0.81	0.85	0.75	0.84	0.55	0.75

2.3. Computational Studies

2.3.1. Absorption: Experiment Versus Calculation

The frontier molecular orbitals for the ground states of **6** and **11** are shown in Figure 8. These two compounds exemplify the major differences in the photophysical behavior of the azafluorenones derivatives. The frontier molecular orbitals for **7**, **9–10**, and **12** are shown in Figures S9–S12. The LUMO (LU) for all the derivatives is approximately the in-phase combination of two e_{2u} benzene LUs with the carbonyl π^* orbital. The HOMOs (HOs) for **6–7** and **9–10** involve lone pair orbitals of the sulfur or nitrogen atom. These are designated as donor (d) orbitals. For **6–7**, **10**, and **12**, the HO−1 is the same as the HO for **11** and is principally an out-of-phase combination of two e_{1g} benzene HOs. For **9**, this orbital is HO−2, but it is nearly degenerate with HO−1. The HO for **12**, in contrast to the rest, is an out-of-phase combination of HOs for the benzene and triazole. Again, because the lone pair on the nitrogen atom connected to the fluorenone is part of the aromatic system, it is not considered a donor like the others. Finally, all have at least one high-lying filled frontier orbital that involves the in-plane carbonyl lone pair. The lone pair on the 4-aza nitrogen is also prominent in these orbitals. For **6–7**, **10**, and **12**, the n-orbital is HO−2, while for **9**, it is HO−1. The ethyl ether **11** is unique in having two close-lying n-orbitals. The relative energies of the frontier orbitals are shown in Figure S13.

**Figure 8.** Frontier molecular orbitals (isovalue: 0.05) for ground states of **6** (top row) and **11** (bottom row).

Nearly all of the long-wavelength absorption transitions are calculated to be primarily HO→LU. Three (**6**, **7**, and **10**) of the four with donor HO orbitals have a small HO−1→LU component mixed in the transition (27:73, 37:63, and 20:80, resp.). Both **9** and **11** have a pure HO→LU transition. Compound **12** has two overlapping transitions. The higher-energy transition is also purely HO→LU, and, unlike the slightly lower-energy transition, it has a non-zero oscillator strength. The calculated absorbance maxima and oscillator strengths are shown in Table 4, along with the experimental results. Calculations correctly predicted that **7** would have the longest-wavelength absorption and the largest extinction coefficient,

while **11** would have the lowest for both. Calculations underestimated the absorption maxima but correctly ordered the molar absorptivities. Except for compound **12**, all of the lowest-energy absorption transitions are $\pi \rightarrow \pi^*$ in nature (Table 5). For compound **12**, the lowest-energy transition is $n \rightarrow \pi^*$.

Table 4. Calculated UV absorption and fluorescence emission wavelengths and oscillator strengths for **6**, **7**, **9–12** in toluene vs. experimental results.

$S_0 \rightarrow S_1$		6	7	9	10	11	12
Calc.	$\lambda_{\max}$ (nm)	361	390	367	380	358	353 ^a
	f	0.065	0.407	0.036	0.102	0.015	0.031
Expt.	$\lambda_{\max}$ (nm)	391	445	387	417	367	370
	$\log \epsilon$	3.82	4.50	3.64	4.02	3.39	3.53
$S_0 \leftarrow S_1$							
Calc.	$\lambda_{\max}$ (nm)	494	505	522	528	512	490
	f	0.012	0.185	0.012	0.027	0.011	0.008
Expt.	$\lambda_{\max}$ (nm)	504	566	528	544	493	491
	Φ_f	0.137	0.877	0.059	0.099	0.0023	0.0005

^a S_2 .

Table 5. Energies (eV) and natures of lowest-lying electronic states for optimized ground states of **6**, **7**, **9–12**.

6				7				9			
2.485	T ₁	$\pi \rightarrow \pi^*$	2.294	T ₁	$\pi \rightarrow \pi^*$	3.136	T ₁	n $\rightarrow \pi^*$			
3.052	T ₂	n $\rightarrow \pi^*$	2.932	T ₂	$\pi \rightarrow \pi^*$	3.229	T ₂	n $\rightarrow \pi^*$			
3.171	T ₃	$\pi \rightarrow \pi^*$	3.175	T ₃	n $\rightarrow \pi^*$	3.379	S ₁	$\pi \rightarrow \pi^*$			
3.436	S ₁	$\pi \rightarrow \pi^*$	3.318	S ₁	$\pi \rightarrow \pi^*$	3.471	T ₃	$\pi \rightarrow \pi^*$			
3.534	S ₂	n $\rightarrow \pi^*$	3.460	T ₄	$\pi \rightarrow \pi^*$	3.615	S ₂	n $\rightarrow \pi^*$			
10				11				12			
2.384	T ₁	$\pi \rightarrow \pi^*$	2.485	T ₁	$\pi \rightarrow \pi^*$	2.522	T ₁	$\pi \rightarrow \pi^*$			
3.121	T ₂	$\pi \rightarrow \pi^*$	3.075	T ₂	n $\rightarrow \pi^*$	3.014	T ₂	n $\rightarrow \pi^*$			
3.164	T ₃	n $\rightarrow \pi^*$	3.333	T ₃	$\pi \rightarrow \pi^*$	3.234	T ₃	$\pi \rightarrow \pi^*$			
3.265	S ₁	$\pi \rightarrow \pi^*$	3.459	S ₁	$\pi \rightarrow \pi^*$	3.508	S ₁	n $\rightarrow \pi^*$			
3.370	T ₄	$\pi \rightarrow \pi^*$	3.565	S ₂	n $\rightarrow \pi^*$	3.514	S ₂	$\pi \rightarrow \pi^*$			

2.3.2. Fluorescence: Experiment Versus Calculation

Electronic transitions for the fluorescence are also primarily between the HO and LU. Again, **6**, **7**, and **10** have HO-1 $\rightarrow$ LU components of similar proportions to the absorption (22:78, 39:61, and 19:81, resp.). Calculations (Table 4) correctly predict that **7** should show the strongest emission but otherwise do not reflect the relative quantum yield ordering. All show emission maxima between 494 and 528 nm. The experimental range from 493 to 566 nm is comparable. Calculations also correctly predict that **12** should have the weakest emission and shortest-wavelength maximum. Table 6 shows the energies and natures of the states for the optimized S_1 structures. The S_1 states are all $\pi \rightarrow \pi^*$.

The fluorescence intensity of the parent 9-fluorenone and its simple derivatives is determined by the competing efficiencies of intersystem crossing (ISC) and internal conversion (IC) [25]. For example, in nonpolar solvents, 9-fluorenone undergoes rapid ISC from an $n \rightarrow \pi^*$ singlet to a $\pi \rightarrow \pi^*$ triplet, resulting in very weak fluorescence. As the polarity increases, the lowest singlet excited state switches to $\pi \rightarrow \pi^*$ and ISC is less effective but is still present [8]. It is thought that forbidden El Sayed processes may be turned on by vibronic spin-orbit coupling [6,7]. For the 4-azafluorenones in this paper, the calculations do not show any obvious route to an efficient El-Sayed ISC ($\pi \rightarrow \pi^*$ singlet to $n \rightarrow \pi^*$ triplet) that

explains the relative fluorescence quantum yields. For the absorption transition (Table 5), the Franck–Condon singlet states of the three amino derivatives (**7**, **9**, **10**) are closer in energy to an $n \rightarrow \pi^*$ triplet state (−3.3, −3.5, and −2.3 kcal/mol, resp.) than the other azafluorenones. However, the amino derivatives fluoresce strongly. For the relaxed singlet excited state (Table 6), the closest $n \rightarrow \pi^*$ triplet state is higher energy, making ISC an endothermic process. The least endothermic of these belongs to **6** (3.1 kcal/mol), but it is the second most fluorescent of the set.

Table 6. Energies (eV) and natures of lowest-lying electronic states for optimized, relaxed singlet excited states of **6**, **7**, **9–12**.

6				7				9			
1.527	T ₁	$\pi \rightarrow \pi^*$	1.567	T ₁	$\pi \rightarrow \pi^*$	1.483	T ₁	$n \rightarrow \pi^*$			
2.511	S ₁	$\pi \rightarrow \pi^*$	2.456	S ₁	$\pi \rightarrow \pi^*$	2.377	S ₁	$\pi \rightarrow \pi^*$			
2.644	T ₂	$n \rightarrow \pi^*$	2.494	T ₂	$\pi \rightarrow \pi^*$	2.709	T ₂	$\pi \rightarrow \pi^*$			
2.713	T ₃	$\pi \rightarrow \pi^*$	2.670	T ₃	$\pi \rightarrow \pi^*$	2.757	T ₃	$n \rightarrow \pi^*$			
3.132	S ₂	$n \rightarrow \pi^*$	3.090	T ₄	$\pi \rightarrow \pi^*$	3.175	T ₄	$\pi \rightarrow \pi^*$			
10				11				12			
1.509	T ₁	$\pi \rightarrow \pi^*$	1.450	T ₁	$\pi \rightarrow \pi^*$	1.545	T ₁	$\pi \rightarrow \pi^*$			
2.353	S ₁	$\pi \rightarrow \pi^*$	2.420	S ₁	$\pi \rightarrow \pi^*$	2.528	S ₁	$\pi \rightarrow \pi^*$			
2.688	T ₂	$\pi \rightarrow \pi^*$	2.631	T ₂	$n \rightarrow \pi^*$	2.591	T ₂	$\pi \rightarrow \pi^*$			
2.741	T ₃	$n \rightarrow \pi^*$	2.816	T ₃	$\pi \rightarrow \pi^*$	2.775	T ₃	$n \rightarrow \pi^*$			
3.097	T ₄	$\pi \rightarrow \pi^*$	3.127	S ₂	$n \rightarrow \pi^*$	3.097	S ₂	$\pi \rightarrow \pi^*$			

3. Conclusions

The synthetic route presented here provides a general and rapid method to prepare 3-substituted 4-azafluorenones from simple and inexpensive reagents. The azafluorenone scaffold is created from ninhydrin, thiomethyl amidrazone, and norbornadiene in two steps. Oxidation provides the common sulfone intermediate **8** for subsequent substitution reactions. The requirement for this route to be effective is that the conjugate base of the desired 3-substituent is a strong nucleophile and gives addition/elimination with the sulfone leaving group rather than nucleophilic addition to the fluorenone carbonyl. Other 3-substituents can be incorporated using a modified amidrazone, as shown with the dimethylaminophenyl azafluorenones **7**.

The photophysical behavior of the 3-substituted 4-azafluorenone derivatives depends on the nature of the substituent. All show several absorption bands above 280 nm. Amino or aminophenyl derivatives have long-wavelength bands between 375 and 500 nm. Thiomethyl, phenoxy, and triazinyl derivatives have bands between 350 and 450 nm. Both the absorption and fluorescence transitions are predicted to be $\pi \rightarrow \pi^*$ and between HO and LU molecular orbitals. Those derivatives with sulfur or nitrogen atom donor groups give medium to strong fluorescence. In these compounds, the donor atom lone pair orbital is a significant part of the HOMO. While phenyl ether **11** has an oxygen atom with a lone pair, the associated lone pair orbital is not a part of the HOMO. The lone pair of the substituted nitrogen of the triazole ring in **12** is part of the aromatic system. Both **11** and **12** fluoresce weakly. The El Sayed rules for ISC deactivation do not easily explain the relative emission intensities. Compound **7** shows much larger solvatochromism than the other derivatives. As a result, **7** also shows strong energy-gap fluorescence quenching due to IC. The greater charge separation through the benzene ring leads to the largest red-shifted fluorescence (741 nm in DMSO) of the set. The other nitrogen atom donor derivatives **9** and **10**, and, to some extent, sulfur atom donor **6**, show H-bond quenching by alcoholic solvents, as seen with 3-aminofluorenones.

4. Materials and Methods

4.1. General

All reactions were carried out under an atmosphere of nitrogen in flame-dried or oven-dried glassware with magnetic stirring unless otherwise indicated. Acetonitrile, THF, toluene, and Et₂O were degassed with argon and purified by passage through a column of molecular sieves and a bed of activated alumina [26]. All reagents were used as received from Thermo Scientific Chemicals (Waltham, MA, USA) or AmBeed (Buffalo Grove, IL, USA) unless otherwise noted. Flash column chromatography was performed using Biotage Sfär Silica D 60 µm on a Biotage Selekt (Upsalla, Sweden) [27]. Analytical thin-layer chromatography was performed on SiliCycle 60Å glass plates (Zeochem Silica Materials, Quebec City, QC, Canada). Visualization was accomplished with UV light, ceric ammonium molybdate, potassium permanganate, or ninhydrin, followed by heating. Infrared spectra were recorded using a Digilab FTS 7000 FTIR spectrophotometer (Hopkinton, MA, USA). ¹H-NMR spectra were recorded on an Agilent DD2-400 spectrometer (Santa Clara, CA, USA) and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm) or tetramethylsilane (0.00 ppm). Proton-decoupled ¹³C-NMR spectra were recorded on an Agilent DD2-400 spectrometer (100 MHz) and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.00 ppm). All compounds were judged to be homogeneous (>95% purity) by ¹H and ¹³C NMR spectroscopy, unless otherwise noted. Mass spectra analysis data was obtained through positive electrospray ionization (w/NaCl) on a Bruker 12 Tesla APEX-Qe FTICR-MS with an Apollo II ion source (Billerica, MA, USA). Absorption and fluorescence data were collected using a fiber optic system with an Ocean Optics Maya2000 Pro CCD detector (Orlando, FL, USA) using an Ocean Optics CHEM200-UV-VIS miniature deuterium/tungsten lamp and an Ocean Optics 365 nm LLS-LED light source, respectively. The Maya spectrometer has a large dynamic range, and the signal intensity can be increased by increasing the sampling time. Cuvettes were thermostated at 23 °C for fluorescence studies. Emission intensities were processed by subtracting the electronic noise, converting wavelengths to wavenumbers (Jacobian transformation), multiplying by $\lambda^2/\lambda_{\max}^2$ to account for the effect of the abscissa-scale transformation [28,29], and dividing by the spectral response of the Hamamatsu S10420 CCD (Saitama, Japan). Relative quantum yields were determined using anthracene (Eastman Organic Chemicals) as the reference ($\Phi = 0.30$) using the method of standard additions.

Electronic structure calculations were conducted using Gaussian 16. Ground-state geometries were optimized using the DFT CAM-B3LYP method employing the 6-311G + (2d,p) basis set with an IEFPCM solvation model for toluene. Excited states were optimized using the TD-DFT CAM-B3LYP method employing the 6-311G + (2d,p) basis set with an IEFPCM solvation model for toluene.

4.2. 3-(Methylthio)-9H-indeno [1,2-e][1,2,4]triazin-9-one (4)

To a dry flask was added 2,2-dihydroxy-1H-indene-1,3(2H)-dione **1** (1.07 g, 6.0 mmol) and EtOH (30 mL). After dissolution, NaHCO₃ (0.58 g, 6.9 mmol) was added, and the mixture was stirred for 5 min before adding the amidrazone salt **2** (1.54 g, 6.6 mmol). The flask was fitted with a condenser and flushed with Ar. The reaction mixture was heated to 100 °C and stirred for 1 h. The reaction mixture was concentrated in vacuo, and the precipitate was collected by suction filtration and washed with water (×3), chilled EtOH, and Et₂O. The resulting residue was dried under vacuum and afforded the 1,2,4-triazafluorenone **4** (1.21 g, 5.27 mmol, 88%) as a brown powder that was used without purification. TLC (40% EtOAc/hexane), *R_f* 0.47; IR (film) 2110, 1755, 1717, 1543, 1422, 1285, 1182 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 8.05 (d, *J* = 6.8 Hz, 1H), 7.95 (d, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.2 Hz, 1H), 2.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ

187.3, 176.4, 162.2, 149.3, 137.9, 136.8, 136.1, 135.3, 125.4, 124.3, 14.8; HRMS (ESI): calcd. for $C_{11}H_7N_3OSNa^+$ 252.0202, found 252.0202.

4.3. 2-(Methylthio)-5H-indeno [1,2-b]pyridin-5-one (6)

To a flask was added **4** (238 mg, 1.04 mmol), PhMe (1.7 mL), and DMF (0.5 mL). The flask was fitted with a condenser and flushed with Ar. Norbornadiene (0.74 mL, 7.28 mmol) was added, and the reaction mixture was heated for 48 h using an aluminum block set to 110 °C (external temperature). The mixture was cooled and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (5–40% EtOAc/hexanes) to give **6** (129 mg, 0.57 mmol, 55%) as an amorphous yellow powder. TLC (20% EtOAc/hexane), R_f 0.74 (UV light); IR (film) 3402, 1707, 1609, 1574, 1557, 1398 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$) 7.80 (d, J = 7.6 Hz, 1H), 7.68 (t, J = 8.0 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 167.4, 165.4, 143.0, 135.3, 134.6, 130.9, 130.6, 123.8, 123.7, 120.7, 120.0, 13.4; HRMS (ESI) calcd. for $C_{13}H_9NOSH^+$ 228.0478, found 228.0477.

4.4. 2-(4-(Dimethylamino)phenyl)-5H-indeno [1,2-b]pyridin-5-one (7)

Gaseous HCl was generated by dripping conc. HCl (100 mL) into H_2SO_4 (100 mL) over 2 h. The liberated gas was bubbled through a H_2SO_4 trap (10 mL) and passed through a $CaCl_2$ tube before bubbling through a solution of dimethylaminobenzonitrile (2.1 g, 14.4 mmol) in CH_3OH (30 mL) held at -10 °C. The mixture was stirred overnight and allowed to warm to room temperature. The contents were poured slowly into diethyl ether (150 mL). The resulting mixture was stirred for 15 min. A solid formed, and the organic liquid was decanted. The solid was collected by suction filtration and washed several times with a small amount of ether. The solid was transferred to a separatory funnel with a small amount of chloroform. Saturated aqueous Na_2CO_3 (100 mL) was added. After the evolution of carbon dioxide subsided, the mixture was extracted with chloroform (2×75 mL). The combined organic layers were dried over $CaCl_2$, filtered, and concentrated in vacuo, leaving 2.15 g of a white solid. This solid was dissolved in isopropanol (25 mL), and the solution was cooled in an ice bath. Hydrazine hydrate (0.75 g, 16.3 mmol) was added slowly, and the reaction was stirred in the ice bath for 1 h. and then allowed to warm to room temperature overnight. The isopropanol was removed in vacuo. The oily residue was washed several times with ether and dried under vacuum (100 torr) for 2 h, leaving 0.85 g of crude amidrazone **3**. This material was combined with ninhydrin **1** (0.85 g, 4.8 mmol) and ethanol (25 mL) and heated to reflux. A black sludge crashed out of solution. Another portion of ethanol (25 mL) was added, and reflux continued for 1 h. After cooling, the crude solid was collected by suction filtration and washed with ethanol (5×25 mL). The filtrate was concentrated in vacuo, leaving 1.33 g of a reddish solid. It was further purified by column chromatography with 15% ethyl acetate/hexanes, giving the crude triazine **5** (0.50 g, 1.7 mmol), which was used without further purification. The triazine (0.24 g, 0.8 mmol) was combined with norbornadiene (1.3 mL, 12.8 mmol) and ethanol (3 mL) and heated to 115 °C for 2 days. The contents were evaporated in vacuo, and the residue was purified by column chromatography with 17% ethyl acetate/hexanes, giving the azafluorenone **7** (90 mg, 0.3 mmol, 38% from the triazine) as a red solid (R_f = 0.48 in 25% ethyl acetate/hexanes). NMR ^1H (400 MHz, $CDCl_3$): 8.10 (d, J = 9.0 Hz, 2H), 7.93 (d, J = 7.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.4, 1H), 7.59 (dd, J = 7.5, 7.4 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 7.5, 7.4 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 3.07 (s, 6H); ^{13}C (400 MHz, $CDCl_3$): δ 191.87, 165.56, 161.99, 151.76, 143.75, 135.77, 134.64, 131.76, 130.59, 128.63, 128.60, 125.08, 123.61, 120.78, 117.60, 112.03, 40.26. HRMS (ESI): calcd. for $C_{20}H_{17}N_2O^+$ [M + H] $^+$ 301.1335; found 301.1336.

4.5. 2-(Methylsulfonyl)-5H-indeno [1,2-b]pyridin-5-one (8)

To a flask was added **6** (304 mg, 1.35 mmol), THF (20 mL), and H₂O (10 mL). Oxone (1.25 g, 4.8 mmol) was added, and the reaction mixture was stirred at rt for 36 h. The reaction mixture was partly concentrated in vacuo to ~10 mL and transferred to a separatory funnel with EtOAc (50 mL) and H₂O (10 mL). The organic portion was removed, and the aqueous portion was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo, affording the methylsulfonyl azafluorenone **8** (252 mg, 0.98 mmol, 72%) as a pale-yellow amorphous powder that was used without purification. TLC (40% EtOAc/hexanes), *R_f* 0.30; IR (film) 1717, 1608, 1589, 1296, 1134 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 8.11 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 3.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.5, 165.5, 161.6, 142.1, 135.9, 135.2, 133.0, 132.3, 131.2, 124.7, 122.1, 120.8, 39.8; HRMS (ESI) calcd. for C₁₃H₉NO₃SNa⁺ 282.0195, found 282.0196.

4.6. 2-Amino-5H-indeno [1,2-b]pyridin-5-one (9)

To a dry vial was added **8** (67 mg, 0.26 mmol), conc. aq. ammonium hydroxide (340 µL, 5.2 mmol), and DMSO (1.5 mL), and the vial was sealed with a pressure-releasing Teflon cap. The reaction mixture was heated at 80 °C for 24 h. The reaction mixture was cooled to rt and transferred to a separatory funnel with EtOAc (80 mL) and H₂O (20 mL). The organic portion was removed, and the aqueous portion was extracted with EtOAc (2 × 40 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (15–100% EtOAc/hexanes) to give **9** (12 mg, 0.06 mmol, 23%) as an amorphous orange powder. TLC (60% EtOAc in hexane), *R_f* 0.55; IR (film) 3406, 2106, 1682, 1638, 1288 cm⁻¹; ¹H NMR (400 MHz, (CD₃)₂CO) 7.56 (m, 4H), 7.46 (t, *J* = 6.4 Hz, 1H), 6.61 (s, 2H), 6.45 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, (CD₃)₂CO) δ 190.7, 168.2, 165.2, 143.8, 137.3, 134.6, 133.6, 131.4, 123.3, 120.7, 118.3, 107.4; HRMS (ESI) calcd. for C₁₂H₈N₂ONa⁺ 219.0529, found 219.0529.

4.7. 2-(Pyrrolidin-1-yl)-5H-indeno [1,2-b]pyridin-5-one (10)

To a dry flask was added **8** (59.2 mg, 0.23 mmol), MeCN (2 mL), and DMF (0.5 mL). Pyrrolidine (21 µL, 0.25 mmol) was added, and the flask was flushed with Ar. The reaction mixture was stirred at rt for 18 h. The reaction mixture was concentrated in vacuo to ~0.5 mL and transferred to a separatory funnel with EtOAc (35 mL) and H₂O (10 mL). The organic portion was removed, and the aqueous portion was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (10–60% EtOAc/hexanes) to give **10** (22 mg, 0.09 mmol, 39%) as an amorphous orange powder: TLC (20% EtOAc/hexanes), *R_f* 0.32; IR (film) 1686, 1570, 1449, 1423 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.86 (d, *J* = 7.0 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 8.6 Hz, 1H), 3.63 (s, 4H), 2.05 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 191.1, 167.2, 160.1, 142.9, 136.9, 133.3, 132.5, 130.5, 122.6, 119.8, 116.3, 104.5, 47.2, 25.3; HRMS (ESI) calcd. for C₁₆H₁₄N₂OH⁺ 251.1179, found 251.1179.

4.8. 2-Phenoxy-5H-indeno [1,2-b]pyridin-5-one (11)

To a dry vial was added **8** (72 mg, 0.28 mmol), K₂CO₃ (39 mg, 0.28 mmol), phenol (29 mg, 0.31 mmol), MeCN (1.5 mL), and DMF (0.5 mL). The vial was sealed with a pressure-releasing Teflon cap, and the reaction mixture was heated to 80 °C for 3 h. The reaction was

cooled to rt and transferred to a separatory funnel with EtOAc (50 mL) and H₂O (10 mL). The organic portion was removed, and the aqueous portion was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (10–80% EtOAc/hexanes) to give **11** (58 mg, 0.21 mmol, 76%) as an amorphous yellow powder. TLC (40% EtOAc/hexanes), *R_f* 0.85; IR (film) 1711, 1566, 1489, 1404, 1263 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) 7.87 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.45 (m, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 190.7, 168.3, 166.1, 153.4, 142.4, 135.4, 134.8, 134.6, 131.0, 129.8, 125.4, 123.7, 123.4, 121.3, 121.0, 109.2; HRMS (ESI) calcd. for C₁₈H₁₁NO₂Na⁺ 296.0682, found 296.0683.

4.9. 2-(1*H*-1,2,4-Triazol-1-yl)-5*H*-indeno [1,2-*b*]pyridin-5-one (**12**)

To a vial was added **8** (100 mg, 0.39 mmol), K₂CO₃ (59 mg, 0.43 mmol), 1,2,4-triazole (29 mg, 0.42 mmol), and DMF (1.5 mL). The vial was sealed with a pressure-releasing Teflon cap. The reaction mixture was stirred at rt for 24 h. The reaction mixture was transferred to a separatory funnel with EtOAc (70 mL) and H₂O (10 mL). The organic portion was removed, and the aqueous portion was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (15–100% EtOAc/hexanes) to give **12** (60 mg, 0.24 mmol, 62%) as an amorphous yellow powder. TLC (60% EtOAc/hexanes), *R_f* 0.53; IR (film) 3115, 2108, 1711, 1573, 1423, 1265 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) 9.29 (s, 1H), 8.13 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 190.1, 165.3, 153.3, 152.6, 142.3, 142.0, 135.3, 135.3, 134.5, 131.7, 127.3, 124.2, 121.2, 111.9; HRMS (ESI) calcd. for C₁₄H₈N₄ONa⁺ 271.0590, found 271.0592.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules31040637/s1>, ¹H and ¹³C NMR spectra of **4**, **6–12** (Figures S1–S8), frontier molecular orbitals of **7**, **9–10**, and **12** (Figures S9–S12), and energies of frontier molecular orbitals for **6**, **7**, and **9–12** (Figure S13).

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Abbreviations

The following abbreviations are used in this manuscript:

ICT	Intramolecular charge transfer
HOMO or HO	Highest occupied molecular orbital
LUMO or LU	Lowest unoccupied molecular orbital
ISC	Intersystem crossing
IC	Internal conversion

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