Syntheses and Photophysical Properties of Fluorescent Dibenzofurans, a Dibenzothiophene, and Carbazoles substituted with Benzoxazole and Hydroxyl Groups to produce Excited State Intramolecular Proton-Transfer

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Dibenzofurans, a dibenzothiophene, and carbazoles, each substituted with a 2-benzoxazolyl group as well as an *ortho*-hydroxyl group, were synthesized to produce fluors with fluorescence due to excited-state intramolecular proton-transfer. The orientations for Friedel-Crafts acylation of 3-methoxydibenzothiophene and of the analogous carbazole were determined. The fluors displayed absorption peaks in the 330-385 nm region with molar extinction coefficients up to 57,000. Fluorescence quantum efficiencies of 0.17-0.44 were obtained at wavelengths that had peak values from 540-600 nm. The fluors are of potential use as wavelength shifters in scintillating polystyrene fibers.

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Introduction.

The properties required of fluors for use in scintillating polystyrene fibers have been described [1-4]. It is now believed that only fluors displaying excited-state intramolecular proton-transfer (ESIPT) will provide adequate light output from fibers >1 m long; conventional fluors, even with large Stokes' shifts, are subject to self-absorption [5]. New ESIPT fluors have been reported recently in the 3-hydroxyflavone family [3,6-7], which may not have adequate stability; in the HBO and HBT classes, which have low fluorescence efficiency [8]; as well as a number of 2,5-dibenzoxazolylphenols, with fluorescence emission maxima at 492-517 nm; and a 2,5-dibenzimidazolylphenol with a fluorescence emission maximum of 478 nm [4].

In order to best match the fluorescence emission of a fluor or shifter to the most transmissive spectral region of radiation-damaged polystyrene, 580 ±20 nm [9-10], and also to match the spectral characteristics of the newest type of photodetector, the CCD, which is likely to have twice the efficiency at 580 nm as at 500 nm [11], ESIPT fluors with peak emission at 580 ±20 nm were sought; these would also be expected to have all the other desirable properties described in the earlier works cited.

When the 2,5-dibenzoxazolylphenols contained a hydroxyl group *para* to the phenolic hydroxyl, that is, 2,5-dibenzoxazolylhydroquinones, a ≈50 nm bathochromic shift in fluorescence emission peak to ≈540 nm resulted, while the monomethyl ether peaked at 580 nm (Table 1, fluors **2-4** in [2]). The extinction coefficient (ε) values were ≈25,000, half the magnitude likely to lead to a fast (≤5 nsec) fluorescence decay time [12]. The low ε values were thought to be a result of steric hindrance to attainment of co-planarity of all aromatic rings in the S_1 state [4]. Simpler HBO derivatives such as 2-(5-methoxy-2-tosylaminophenyl)benzoxazole also showed greater bathochromic shifts of both absorption and fluorescence bands than analogs without the presence of a methoxy group *para* to the proton-donating group [13]. After the present work was complete, we became aware that a related benzimidazole ("DiMe-3" in [14] containing a carboxylate ester group in the same location as the second benzoxazole group in the dibenzoxazoles) displayed long-wave absorption at 380 nm and ESIPT fluorescence at 570 nm with $\Phi_f = 0.20$; without the ester group the long-wave absorption in dioxane was 341 nm, the ESIPT fluorescence at 530 nm, but with $\Phi_f = 0.48$ [15].

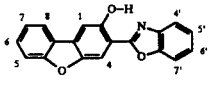
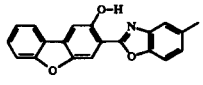
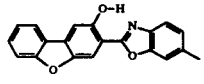
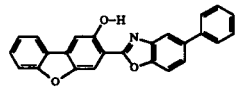
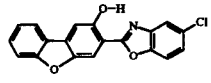
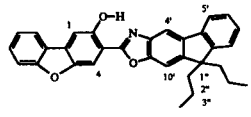
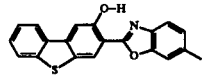
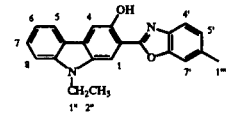
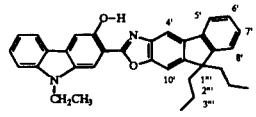
Discussion and Results.

Overall Rationale.

To obtain the longer emission wavelengths, the presence of an oxygen atom *para* to the proton-releasing phenol was thought necessary, especially as part of a stable ether function. The absence of quenching groups such as the ester group was desirable. One approach toward elimination of undesirable steric effects as well as minimizing the chances of collisional deactivation was to incorporate the ether function into a dibenzofuran system as in 3,6-bis(2-benzoxazolyl)-2-hydroxydibenzofuran. As its synthesis seemed too formidable, we decided to make, as a model compound, the mono benzoxazolyl dibenzofuran **4A** (Scheme 1). Its fluorescence emission peak in toluene solution was found to be 545 nm, a ≈50 nm bathochromic shift from those of the 2,5-dibenzoxazolylphenols, despite

Table 1

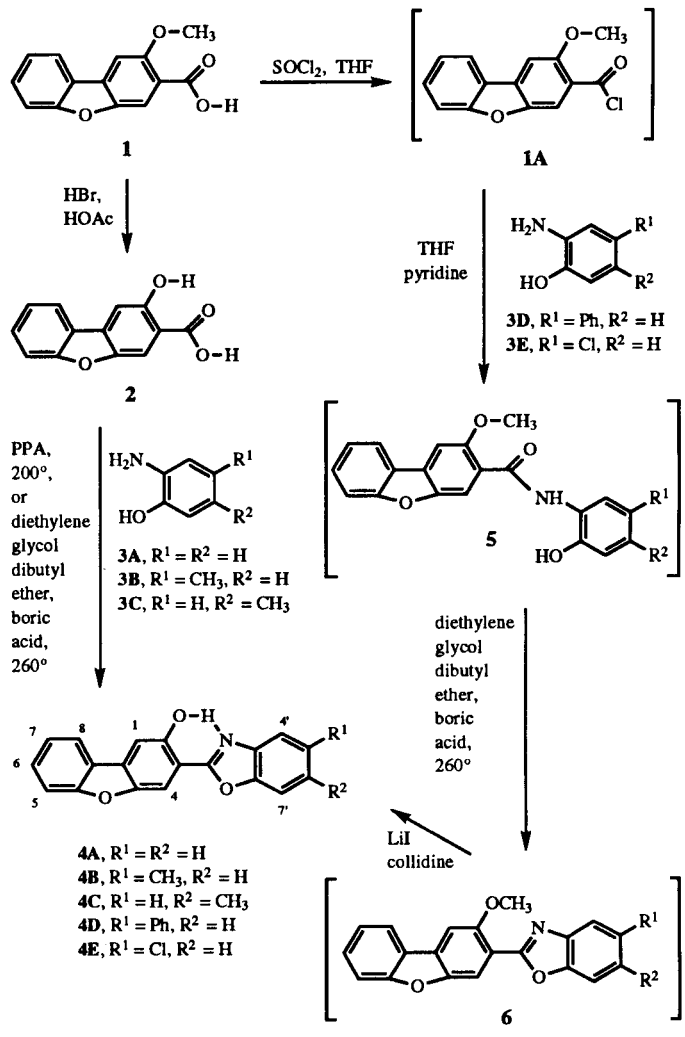
Photophysical Properties of Dibenzofurans, a Dibenzothiophene, and Carbazoles substituted with Benzoxazole and Hydroxyl Groups

No.	Structure	λ max [a]	ε	λ fl em	Φ [a]
4A		318nm	34,000	545 nm	0.36
		333	47,000		
		358	26,000		
		376	28,000		
4B		283	9,700	545	0.41
		320	26,000		
		335	37,000		
		360	23,000		
		377	25,000		
4C		283	29,000	545	0.41
		304	22,000		
		319	33,000		
		335	45,000		
		359	28,000		
		378	31,000		
4D		323	32,000	544	0.41
		337	46,000		
		360	33,000		
		380	35,000		
4E		323	36,000	545	0.32
		337	49,000		
		360	33,000		
		379	34,000		
15		315	22,000	543	0.44
		329	24,000		
		345	42,000		
		369	49,000		
		389	54,000		
24		331	41,000		
		347	40,700	565	0.36
		370	9,700		
		388	12,900		
47		346	48,000	598	0.17
		362	41,000		
		401	6,700		
		420	8,200		
49		321	14,000	598	0.21
		360	57 000		
		375	48,000		
		423	11,000		

[a] In toluene at 20°.

Scheme 1

Synthesis of 3-(2-benzoxazolyl)-2-hydroxydibenzofurans



the smaller size of the new fluorophore.

To determine how much further the fluorescence emission could be shifted bathochromically, we wanted to prepare an *N*-alkylcarbazole in order to have, in place of the oxygen atom in the dibenzofuran, the heteroatom with the most electron-releasing ability that is also the least likely to quench fluorescence—nitrogen. For a time we were unable to synthesize an appropriate carbazole; therefore, we prepared the dibenzothiophene **24** (Scheme 3), since sulfur is more electron-releasing than oxygen. In **24** the fluorescence emission peak was bathochromically shifted to 565 nm. Efforts to prepare the corresponding carbazole (**47**, Scheme 5) thus seemed warranted, and eventually succeeded; its emission peak was ≈600 nm.

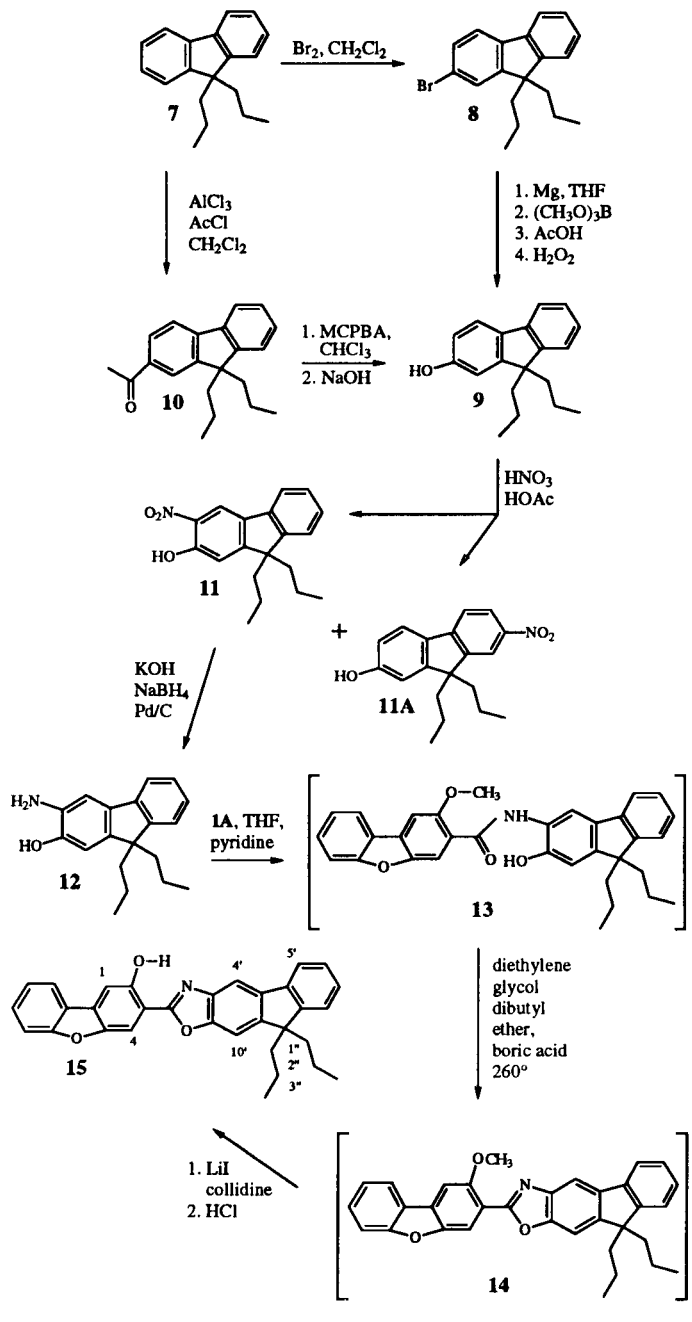
Placement of methyl groups on the 5- or 6-positions of the benzoxazole moiety of the dibenzofurans had significant effects on the photophysical properties, but placement of chloro and phenyl groups in the 5-position had no greater effect. Forcing the 5-phenyl group into the plane of the benzoxazole system by use of a methylene bridge (making a fluorene system) gave a dibenzofuran (**15**, Scheme 3) and a carbazole (**49**, Scheme 5) with higher values of ε and Φ (Table 1).

Syntheses.

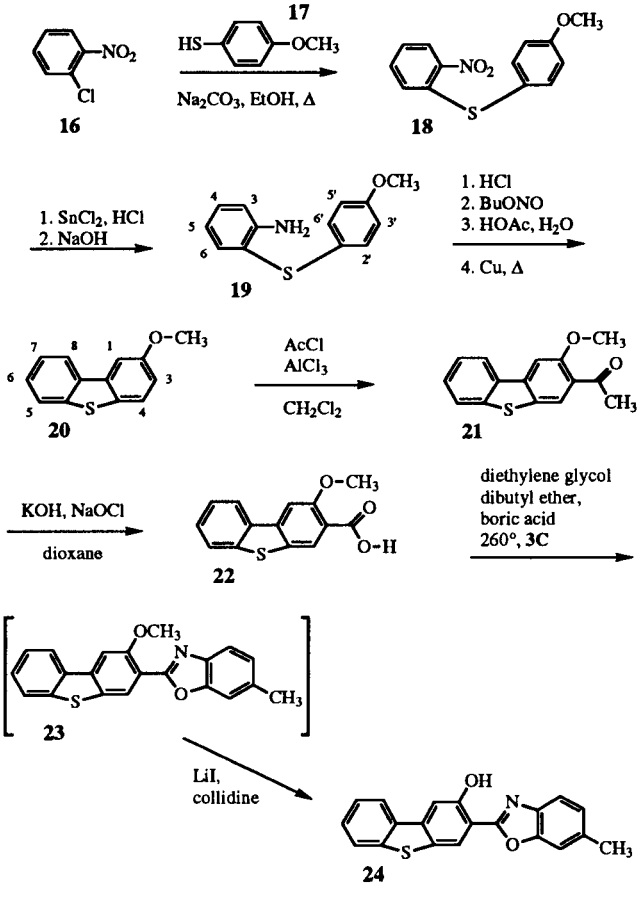
Dibenzofurans.

Friedel-Crafts acetylation of 2-methoxydibenzofuran was shown to give the 3-acetyl derivative by hypohalite

Scheme 2
Synthesis of 3-(9,9-dipropylindeno[3,2-*f*]-2-benzoxazolyl)-2-hydroxydibenzofuran



Scheme 3
Synthesis of 2-hydroxy-3-(6-methyl-2-benzoxazolyl)dibenzothiophene

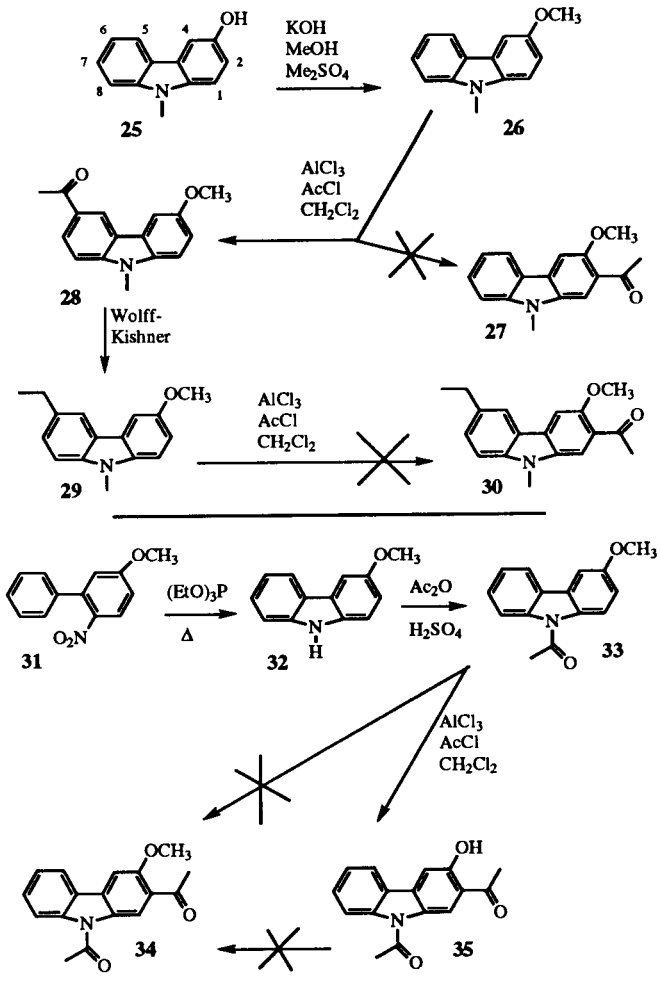


oxidation to the known acid **1** [16]. Demethylation of **1** by means of hydrobromic acid gave the new 2-hydroxydibenzofuran-3-carboxylic acid **2**, whose pmr spectrum showed the same chemical shift for the 2 exchangeable protons. Direct reaction of **1** with aminophenols **3A-3C** gave low yields of the benzoxazoles **4A-4C**, whether in polyphosphoric acid (PPA) at 200° [2] or by distilling out by-product water, as it was formed, from a mixture with the solvent 2-butoxyethyl ether. Much higher yields were reported for some 2,5-dibenzoxazolylhydroquinones with PPA at 180-200° in a paper uncovered when this work was complete [14]. This may have been due to the use of twice as much PPA as we used, or a result of greater sensitivity of hydroxydibenzofurans to hot PPA.

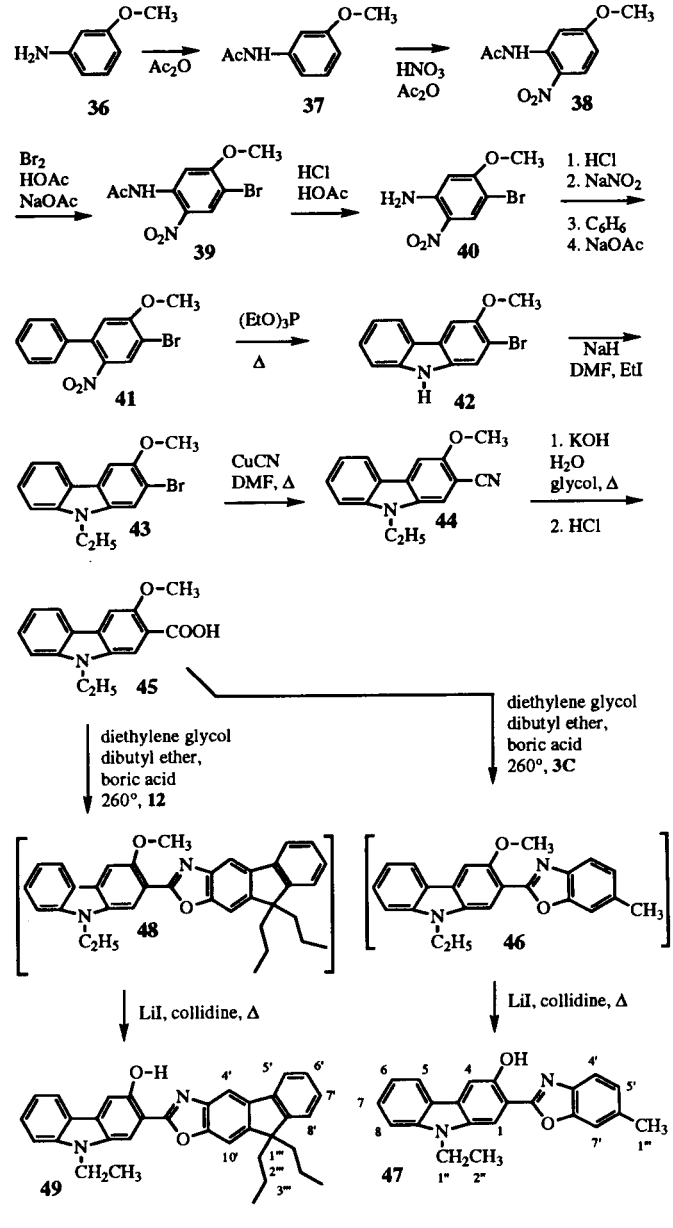
The 2-hydroxy group of the dibenzofuran was thought to interfere with benzoxazole formation; therefore, in all later work, the 2-hydroxy was carried along protected as the methyl ether until the last step. In addition, the amides such as **5** were formed and isolated, but not purified. Thus the acid **1** was converted to the acid chloride **1A**; the amides were formed with aminophenols **3D** and **3E**; the crystalline amides **5** were heated in 2-butoxyethyl ether with boric acid catalyst to give a crystalline mixture of benzoxazole **6** with some demethylated benzoxazole **4**. Demethylation was completed by means of lithium iodide in refluxing collidine [17] since oxazoles are supposed to be subject to decomposition in hot mineral acids [18]; however, this supposition was not checked.

The 200 MHz pmr spectrum of **4E** was resolved well enough to show that the H4 singlet in acid **2**, δ 8.1 at 60 MHz, was further shifted upfield to 8.23 ppm (the *para*

Scheme 4
Attempted Preparations of 3-(2-benzoxazolyl)-3-hydroxycarbazoles



Scheme 5
Successful Preparations of 3-(2-benzoxazolyl)-3-hydroxycarbazoles



splitting being too small to be seen). This shift is similar to that of H3 in 2,5-bis(5-*t*-butyl-2-benzoxazolyl)phenol (**11** in [2]), 8.16 ppm, each being the most deshielded aromatic proton.

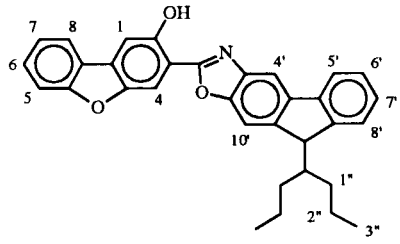
For the synthesis of dibenzofuran **15** (Scheme 2) the aminophenol **12** had to be constructed. Bromination of 9,9-dipropylfluorene **7** gave the 2-bromo derivative **8**, which is especially difficult to separate from the 2,7-dibromo [19]. Grignard reaction of **8**, followed by *in situ* reaction with trimethyl borate, then with hydrogen peroxide, gave the phenol **9**. We have since found that acetylation of 9,9-dipropylfluorene to the 2-acetyl **10**, followed by a Baeyer-Villiger reaction to give phenol **9**, is superior overall. Nitration of **9** gave the expected isomers **11** and **11A**. The more soluble **11** was obtained pure by passage through Silica Gel. Reduction to the aminophenol **12** was straightforward, and was followed by formation of amide **13** by reaction with **1A**, formation of benzoxazole **14**, and demethylation with lithium iodide to obtain the ESIPT fluor **15**. It was possible to assign δ values in the pmr spectrum for every proton in **15** (Figure 1).

Dibenzothiophene.

Hori *et al.* [20] described a synthesis of 2-methoxydibenzothiophene **20** that began with monobromination of dibenzothiophene. In our hands the bromination did not yield a pure product. Instead, we proceeded according to Scheme 3, beginning with reaction of *o*-chloronitrobenzene **16** with the sodium salt of 4-methoxythiophenol **17** to give the diphenyl sulfide **18** according to a procedure for the desmethoxy compound [21]. While catalytic reduction of the desmethoxy compound has been

Figure 1

Interpretation of ^1H NMR (Varian XL 200 MHz) Spectrum of 3-(9,9-Dipropylindeno[3,2-*f*]benzoxazol-3-yl)-2-hydroxydibenzofuran (**15**)



H assignments	δ (ppm)	# of Hs	multiplicity	J = Hz
1	7.65	1H	d	1, 4 0.4
4	8.19 [a]	1H	d	5, 6 8.4
5	7.580	1H	ddd	5, 7 1.7
6	7.52	1H	ddd	5, 8 0.8
7	7.34 [b]	1H	not determ.	6, 7 6.8
8	7.97	1H	ddd	6, 8 1.4
4'	8.01	1H	d	7, 8 7.7
5'	7.78	1H	cm	
6', 7', 8' [c]	7.33-7.42	1H	not determ.	
10' [c]	7.61	1H	d	4', 10' 0.7
1"	2.03	4H	cm	1", 2" ~7.5
2"	0.68	4H	s	
3"	0.68	6H	s	
OH	11.53	1H	broad s	

[a] H4 has much longer T_1 than other ring hydrogens due to isolation. [b] Shift determined from COSY plot. [c] Assignments made with help of COSY and measured nOe enhancement of H8' and H10' during one dimensional nOe difference spectroscopy using a Varian DOCYCL pulse package to selectively excite H1". Sample was de-gassed in a J. Young valve nmr tube (Wilmad) using five freeze-thaw cycles under vacuum.

[22], it failed in our hands, so we used a tin(II) chloride reduction [23] to obtain amine **19** in up to 92% yield. Diazotization and coupling to give 2-methoxydibenzothiophene **20** in poor yield was modeled on a known method [24]. Our melting point was significantly higher than that reported (57.3-58.8° *vs.* 54-55°). The pmr spectrum showed the proton on C3 furthest upfield with a clear *ortho/meta* splitting pattern, the proton on C4 with an *ortho/para* pattern, and the proton on C1 with a *meta* doublet. Friedel-Crafts acetylation gave a clean acetyl compound in 55% yield as shown by the pmr spectrum, in which resonance assigned to the proton on C3 was not seen, the proton on C4, now a singlet, was shifted furthest downfield, and the proton on C1, now a singlet, was shifted slightly upfield, all in agreement with structure **21**. A haloform reaction gave the acid **22**, which was converted to the benzoxazole **23**, and this ether was demethylated with lithium iodide to give the ESIPT fluor **24**.

Carbazoles.

While 3-hydroxy-9-methylcarbazole-2-carboxylic acid has been reported as obtainable from 3-hydroxy-9-methylcarbazole **25** [25] by reaction with carbon dioxide, we could not repeat this Kolbe reaction.

The phenol **25** (Scheme 4) [26] was methylated to form the ether 3-methoxy-9-methylcarbazole **26**, for which the pmr spectrum showed the most upfield proton, the proton on C2, to be a doublet with *ortho* splitting, resembling the proton on C3 in dibenzothiophene **20**. The proton on C1 showed *ortho/para* splitting; the proton on C4 showed *meta/para* splitting; and the most downfield proton was the proton on C5 with *ortho/meta/para* splitting. Friedel-Crafts acetylation gave a mixture of isomers which gave a single pure product in 29% yield, mp 140.5-142.5°; this was shown not to be **27**, but to be **28**, as the protons on C1, C2 and C4 were nearly unchanged in the pmr spectrum, while the proton on C5 was shifted still further downfield to 8.65 ppm with *meta/para* splitting, and the proton on C7 was shifted downfield to 8.07 ppm with *ortho/meta* splitting; all protons were well-resolved and assigned. It was decided to reduce the acetyl group to an ethyl group to form **29**, allow the ethyl group to block C6, and acetylate again to obtain **30**. For reasons not apparent, the ketone **30** was not obtained, starting material being recovered.

Reductive cyclization of 5-methoxy-2-nitrobiphenyl **31** [27] by means of triethyl phosphite gave 3-methoxycarbazole **32** in fair yield; there was no advantage to the use of tris(trimethylsilyl)phosphite [28]. *N*-Acetylation gave **33**; such substitution has been reported to change the orientation of electrophilic substitution to the 2-position [29], which should have been reinforced by the directive influence of the 3-methoxy group. Such was the case when a Friedel-Crafts acetylation was carried out on **33**; however, the expected ether **34** was not obtained, but the demethylated phenol **35** instead. This was caused by the large excess of aluminum chloride necessary to bring about the acylation; such ether cleavages are well known [30]. Re-methylation of the phenol by standard methods did not succeed.

Thus we were driven to constructing a carbazole **42** with groups in *both* the 2- and 3-positions that could be converted to the desired functional groups as in **45**. Reaction of *m*-anisidine **36** with acetic anhydride gave the acetanilide **37**, nitration of which gave the expected isomer mixture [31], from which the more soluble isomer **38** was obtained easily by extraction from alumina in an Ace-Kauffman Column. Bromination gave **39**, whose structure was shown by its pmr spectrum, in which the two aromatic protons are two singlets at 8.4 and 8.6 ppm. Hydrolysis gave the amine **40**, whose pmr spectrum showed the two singlets at 6.5 and 8.2 ppm, further supporting the structure. Diazotization and Gomberg coupling of amine **40** with benzene gave biphenyl **41** in 61% yield. Reductive cyclization gave carbazole **42** in 20% yield; this was *N*-

ethylated to give **43**, whose structure was confirmed by its pmr spectrum, in which the resonances of the upfield proton on C2 seen in **25** were not present. The protons on C1 and C4 appeared as singlets at 7.58 and 7.59 ppm. The proton on C5 remained the furthest downfield, 8.03 ppm with *ortho/meta/para* splitting. The bromine atom in **43** was displaced by a cyano group to give **44**, whose hydrolysis gave the acid **45**. This, with the appropriate amines, **3C** and **12**, was converted to benzoxazoles **46** and **48**; these were demethylated to the ESIPT fluors **47** and **49**. These carbazoles were more soluble in toluene and chloroform than the corresponding dibenzothiophene and dibenzofurans; we attribute this to the presence of the *N*-ethyl group in the carbazoles.

Photophysical Properties (Table 1).

The prototype molecule with a single benzoxazole group for this class of ESIPT fluors is 2-(2-hydroxyphenyl)benzoxazole (HBO) which shows a single "longwave" ultraviolet absorption at 330 nm (ε = 13,000) and a weak emission at 490 nm [2]. The new fluors **4A-4E** (Table 1) all show a corresponding maximum at 333-337 nm (ε = 37,000-49,000) with strong emission at 545 nm. Under long-wave ultraviolet excitation these materials showed (to the naked eye) an intense fluorescence in the solid state, or in solution, or in contact with water, with very little daylight-excited fluorescence; the apparent colors were yellow-green for the dibenzoxazoles, yellow-orange for the dibenzothiophene, and deep orange for the carbazoles. All the fluors show an exceptionally large Stokes' shift (SS). Using the absorption band with the highest value of ε to calculate the SS, values of 202 nm are seen for the dibenzofurans **4A-4E** and 237 nm for the carbazoles **47** and **49**. The commonly used ESIPT fluor 3-hydroxyflavone, by comparison, has a SS of 188 nm.

Replacement of the oxygen atom in dibenzofuran **4C** by a sulfur atom in **24** bathochromically shifted the emission peak 20 nm; by a nitrogen atom in carbazole **47** 53 nm. This was echoed by dibenzofuran **15** and carbazole **49**—a 55 nm shift was seen. The absorption (or excitation) peaks do not shift as much. This must mean that the S_1' state from which emission takes place is of lower energy in proportion to the ability of the key heteroatom to bear a positive charge. The hypothesized electron movement is shown in Figure 2. In earlier work we postulated similar patterns of π-electron flow for benzoxazoles [2] and for flavones [3] in which the outermost two pairs of π-electrons on the benzo groups were not involved. Similar electron flow has now been demonstrated for benzimidazoles by showing the similarity of their spectra to those of related imidazoles with ESIPT fluorescence [15].

The substitution of a methyl group in **4B** by a phenyl group in **4D** had no significant effect on any of the photophysical properties. Making aromatic rings in an oligophenylene-like molecule co-planar by use of a methylene bridge nearly always creates a larger effective fluorophore [3,32]. Alkylation of the methylene "bridge" in fluorenes with propyl groups eliminates the reactive benzylic hydrogens and also provides an important improvement in solubility. Such was the case with **15** *vs.* **4D** and with **49** *vs.* **47**, since new longer-wavelength absorption peaks with the highest ε values appeared. Chernova *et al.* [13] speak of certain intense absorption bands in 2-phenylbenzoxazoles as due to a chromophore that is isoelectronic with stilbene. The corresponding chromophore in **15** and **49** is isoelectronic with 1,2-bis(2-fluorenyl)ethene. The nearest non-ESIPT fluors we know of containing a related chromophore, a pair of 1,4-bis(2-fluorenyl)benzenes, have long-wave bands at 332 nm [33], much shorter than the 369 and 389 nm bands of **15** and the 375 nm band of **49**. At present we cannot account for the origin of these bands.

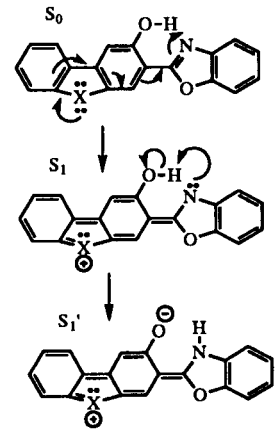


Figure 2. Hypothesized electron flow and charge distribution in lowest energy excited states of the ESIPT fluors of this work.

Some classes of ESIPT fluors, including the 3-hydroxyflavones, do not retain their Φ_f in protic solvents or at higher temperatures [3]. The ESIPT fluors presented here retain much of their Φ_f under such conditions. We think that is because these benzoxazoles have strong hydrogen-bonding, forming a 6-membered ring, even in the ground state. This hypothesis is supported by the difference in δ values for the phenolic protons—7.1 ppm from tms for at least 2 of the 3-hydroxyflavones *vs.* 11.2-11.5 for 3 of these benzoxazoles.

While these benzoxazoles are very stable thermally and survive polymerization in styrene, they partially decompose to form a tan impurity on Silica Gel or in tetrahydrofuran solution when exposed to long-wave (365 nm) light for a few hours.

The scintillation properties of some of these fluors when incorporated into polystyrene are reported elsewhere [8].

Conclusions.

Both 2-methoxydibenzofuran and -thiophene were acetylated in the 3-position, while, under similar Friedel-Crafts conditions, 9-ethyl-3-methoxycarbazole was acetylated substantially in the 6-position.

Incorporation into an aromatic ring system of an ether function *para* to the proton-donating phenolic hydroxyl group not only gave the predicted emission peak at ≈540 nm for the dibenzofurans, but gave fluors with unexpectedly high Φ_f.

The 3-(2-benzoxazolyl)-2-hydroxydibenzofurans and -dibenzothiophene as well as the analogous 2-(2-benzoxazolyl)-3-hydroxycarbazoles are thermally stable ESIPT fluors displaying high fluorescence efficiency (FE = $\Phi_f \cdot \varepsilon$), and a larger SS (by 50 nm) than the 2,5-dibenzoxazolylphenols. The larger SS is due mainly to more bathochromically shifted emission (see Figure 3 as a typical example). The progressively longer wavelengths of both absorption and fluorescence for these compounds, from oxygen to sulfur to nitrogen, seem correlated to the ability of these heteroatoms to support a positive charge in the excited state. For HBO the FE = 221 [2]; for the most efficient flavone reported the FE = 28,000 [3]; for dibenzofuran **15** the FE = 24,000; and for carbazole **49** FE = 12,000. The unusually high SS and emission wavelength (598 nm) shown by the carbazoles **47** and **49** may be of value when CCD light detectors are used.

These emission wavelengths were the longest yet observed from proton-transfer fluors of comparably high thermal and chemical stability, as well as reasonable FE at room temperature, even in the presence of protic solvents, and a large SS. The fluors are not as photochemically stable as the 2,5-dibenzoxazolylphenols. The fluors are of potential use as wavelength shifters in scintillating polystyrene fibers, and in other applications in which uv-induced fluorescence is desired with no visible fluorescence under visible light.

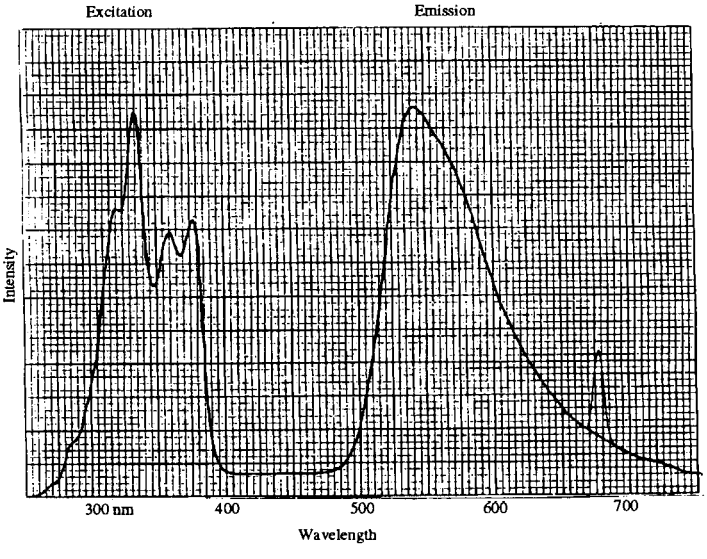


Figure 3. Fluorescence Spectrum of 2-Hydroxy-3-(6-methyl-2-benzoxazolyl)dibenzofuran **4C** in toluene at ≈3 x 10^{-6} *M*.

EXPERIMENTAL

General.

Our methods were similar to those described [4], except that infrared spectra were determined with a Perkin-Elmer 283 grating instrument in chloroform as the solvent, except for those determined in a Diffuse Reflectence Cell (DRC) in which case a Perkin Elmer 1600 Series FTIR was used. Interpretations were based on Vogel's Text [34]. The 60 MHz pmr spectra were determined with a Varian EM360L and made use of deuteriochloroform as the solvent unless specified otherwise. The pyridine was Distilled-in-Glass from Burdick & Jackson, used without further drying; the 2-butoxyethyl ether (also called Dibutyl Carbitol™ and diethylene glycol dibutyl ether) was Aldrich 20,562-1; the alumina was Br. I (neut.), Aldrich 19,997-4; the Silica Gel™ was Aldrich 24,217-9 (equivalent to Merck 10181); the anhydrous lithium iodide was Aldrich 21,821-9, 99%; and the 2,4,6-collidine was Aldrich 14,238-7, 99%. The absorption and fluorescence spectral data are in Table 1.

Dibenzofurans.

2-Hydroxydibenzofuran-3-carboxylic Acid **2**.

A mixture of 2-methoxydibenzofuran-3-carboxylic acid (1,21.62 g, [16]), 48% hydrobromic acid (250 ml) and acetic acid (175 ml) was boiled under reflux for 2 hours, allowing bromomethane to escape, removed from the heat source, diluted with 400 ml of water while stirring, and cooled in ice to 30°. The crystalline product was filtered, washed with water, and dried, to give 19.9 g (98%), mp 301-302° dec. An analytical sample was prepared by twice recrystallizing a portion from 2-ethoxyethanol, mp 301-303° dec; pmr (60 MHz, 5% in DMSO-d_6): δ = 7.3-7.7 (3H, m, H5, H6, H7), 7.79 (1H, s, H1), 8.1 (1H, s, H4); 8.2 (1H, d, $J_{7\text{-}8}$ = 6 Hz, H8); 11.27 (2H, br s, -O*H*s).

Anal. Calcd. for $C_{13}H_8O_4$: C, 68.42; H, 3.54. Found: C, 68.57; H, 3.58.

2-Hydroxy-3-(2-benzoxazolyl)dibenzofuran **4A**.

The acid **2** (4.40 g) was ground in a mortar with 2-aminophenol (**3A**, 2.11 g, see p1618 in [2]) and the mixture was added to 40 ml of polyphosphoric acid at ≈100°, then held at 200° for 16 hours, cooled to ≈100°, and quenched in a mixture of 250 g of ice and 150 g of water. The *p*H was lowered to 3 with 19 *M* sodium hydroxide, and the crude product was filtered and dried to give 3.19 g of sticky solid. This was extracted from a small Soxhlet with 150 ml of toluene. The cooled extract was passed thru Br. I alumina, which was further eluted with 300 ml of toluene and 400 ml of dichloromethane to give, on evaporation, a solid, which was recrystallized from 25 ml xylenes to give 0.36 g of product, mp 267-270°. This was recrystallized from 35 ml of 2-ethoxyethanol to give 0.32 g (6%) of needles, mp 269-270°. The solubility in xylenes was 1.2 g/L or 4.1 x 10^{-3}*M*.

Anal. Calcd. for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65. Found: C, 75.12; H, 3.44; N, 4.72.

2-Hydroxy-3-(5'-methyl-2-benzoxazolyl)dibenzofuran **4B**.

A mixture of 2-hydroxydibenzofuran-3-carboxylic acid (**2**, 4.56 g), 2-amino-4-methylphenol (**3B**, 2.46 g), 25 ml of 2-butoxyethyl ether, and 0.20 g of boric acid was heated at 170° overnight, then more strongly so that half the solvent distilled during ≈2 hours. When the residue reached 20° it was filtered, the black solid was washed with 50 ml of 2-propanol, then dried, to give 1.83 g. This was extracted from 4 cm of Silica Gel under 2 cm of Br. I alumina in a small Ace-Kauffman column with 80 ml of toluene until all fluorescent material was extracted; the extract was kept at -20°, filtered, and the solid was washed with 25 ml of 95% ethanol and dried to give 0.78 g of material, which was recrystallized from 32 ml of 2-ethoxyethanol, yielding 0.60 g (10%) of pink needles, mp 248-250°.

Anal. Calcd. for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.15; N, 4.44. Found: C, 76.11; H, 4.05; N, 4.33.

2-hydroxy-3-(6'-methyl-2-benzoxazolyl)dibenzofuran **4C**.

A mixture of 2-hydroxydibenzofuran-3-carboxylic acid (**2**, 4.56 g), 2-amino-5-methylphenol (**3C**, 2.46 g), 25 ml of 2-butoxyethyl ether, and 0.20 g of boric acid was treated as above. The toluene extract was diluted with half its volume of methanol before cooling to -20° to obtain pink needles, 0.068 g (1.1%) mp 242-242.5°.

Anal. Calcd. for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.15; N, 4.44. Found: C, 75.98; H, 3.98; N, 4.31.

2-Hydroxy-3-(5-phenyl-2-benzoxazolyl)dibenzofuran **4D**.

A mixture of 3-carboxy-2-methoxydibenzofuran (**1**, 8.88 g, 36.7 mmoles), 50 ml of dry tetrahydrofuran, 2.81 ml (38.5 mmole) of thionyl chloride, and 0.1 to 0.2 ml of *N*-methylpyrrolidinone under nitrogen was boiled under reflux for 2.5 hours and then allowed to cool to room temperature. Meanwhile, a solution of 2-amino-4-phenylphenol (**3D**, 7.13 g, 38.5 mmoles, TCI A0397), 50 ml dry tetrahydrofuran, and pyridine (6.23 ml, 77 mmoles) was prepared under nitrogen. To this solution was added the cooled acid chloride **1A** solution during several minutes, resulting in an exotherm to 40° and the formation of a precipitate. The mixture was stirred for an additional hour, quenched by pouring it into 400 ml of water, and made acidic (*p*H ~1). The solid was collected by vacuum filtration, washed with water, slurried in 500 ml of methanol, re-filtered, and washed with an additional 200 ml of methanol, to give a brown solid. The solid was again slurried in 200 ml of methanol, filtered, washed with 50 ml of methanol, and dried (90°/30 torr/2 days), to give 9.53 g (64%) of *N*-(4-hydroxy-3-biphenylyl)-2-methoxydibenzofuran-3-carboxamide **5D**, mp 227.5-230.5°, dark melt or dec; ir (potassium bromide, DRC): ν 3304 (NH), 3102 (OH), 2941, 1629 (C=O), 1610 (C=C), 1549 (NH), 1513, 1489, 1465, 1452, 1425, 1361, 1308, 1282, 1261, 1221, 1193, 1169, 1121, 1077, 1029 (OCH_3), 904, 856, 838, 814, 761, 746, 700.

Into a 100 ml, 2-necked, round-bottomed flask, equipped with magnetic stirring, nitrogen inlet, a thermometer dipping into the solution, and a combination distillation head/air condenser, were placed the amide **5D** (9.00 g, 22.0 mmoles), 0.23 g of boric acid and 36 ml of 2-butoxyethyl ether. The mixture was heated slowly (45 minutes) to reflux (255-260°), held at this temperature for 1/2 hour, and then ~2/3 (20-24 ml) of the solvent was removed by distillation. The remaining solution was cooled to ~80° and poured into 100 ml of heptane, resulting in the formation of a semisolid. The mixture was boiled to break-up the solid and then cooled to -20°. The dark brown solid obtained was filtered, washed with 25 ml heptane and dried (90°/1 hour/30 torr) to give 8.36 g (97%) of solid. The solid was placed in a medium Ace-Kauffman column over 4 cm alumina and extracted with heptane. Once most of the fluorescent material had been eluted, the pot was cooled to -20°, the solid was filtered and dried (1.5 hours/70°) to give 5.48 g (64%) of 2-methoxy-3-(5-phenyl-2-benzoxazolyl)dibenzofuran **6D**, mp 155-160°, res.

A mixture of the methoxydibenzofuran **6D** (5.2 g, 13 mmoles), lithium iodide (3.12 g, 23.4 mmoles) and 20 ml of collidine under nitrogen was boiled under reflux for one hour during which time the mixture thickened. The mixture was cooled somewhat and poured into 150 ml of 3 *M* hydrochloric acid. An additional 100 ml of water was added and the mixture was stirred at room temperature for 1/2 hour. The resulting solid was collected by filtration, washed with water and dried (16 hours/80°) to give 5.05 g of solid. The solid was placed in a medium Ace-Kauffman column over 4 cm alumina and extracted with ethyl acetate. Once all fluorescent material had been eluted, the pot was cooled to room temperature, the solid collected by filtration, washed with 30 ml ethyl acetate and dried (70°/5 hours) to give 4.69 g (94%) of pale yellow **4D** mp 293-295°, shrinks 291°.

Anal. Calcd. for $C_{25}H_{15}NO_3$: C, 79.56; H, 4.01; N, 3.71. Found: C, 79.57; H, 4.06; N, 3.66.

3-(5-chloro-2-benzoxazolyl)-2-hydroxydibenzofuran **4E**.

A nitrogen-blanketed mixture of 3-carboxy-2-hydroxydibenzofuran (**2**, 10.00 g, 41.3 mmoles), 50 ml of dry tetrahydrofuran, thionyl chloride (3.17 ml, 43.4 mmoles, Aldrich 23,046-4), and 0.1 to 0.2 ml of *N*-methylpyrrolidinone was boiled under reflux for 2.5 hours, allowed to cool to room temperature, and added to a mixture of 2-amino-4-chlorophenol (**3E**, 6.23 g, 43.4 mmoles, Aldrich C4,440-0), 50 ml dry tetrahydrofuran, and 7.01 ml pyridine over several minutes, resulting in an exotherm to 40° and the formation of a precipitate. The mixture was stirred overnight, quenched in 400 ml of water, and made acidic (*p*H ~1). The solid was collected by vacuum filtration, washed with water, slurried in 200 ml of methanol, refiltered, washed with an additional 50 ml of methanol, and dried (16 hours/100°), to give 9.9 g (65%) of *N*-(2-hydroxy-5-chlorophenyl)-2-methoxydibenzofuran-3-carboxamide **5E**, mp 257-259°; ir (potassium bromide, DRC): ν 3300 (NH), 3205 (OH), 1632 (C=O), 1610 (C=C), 1549 (NH), 1494, 1462, 1450, 1426, 1360, 1305, 1265, 1243, 1222, 1195, 1184, 1164, 1121, 1027 (OCH_3), 869, 854, 810, 738, 656, 646.

Into a 100 ml, 2-necked, round-bottom flask, equipped with magnetic stirring, nitrogen inlet, thermometer dipping into the solution, and a combination distillation head/air condenser, were placed the amide **5E** (9.00 g, 24.5 mmoles), boric acid (0.25 g, 4.0 mmoles) and 36 ml of 2-butoxyethyl ether. The mixture was heated slowly (45 minutes) to reflux (255-260°), held at this temperature for 1/2 hour, and then ~2/3 (25 ml) of the solvent was removed by distillation. The remaining solution was cooled to ~80° and poured into 100 ml of heptane, resulting in the formation of a solid. The mixture was boiled to break up the solid and then cooled to -20°. The tan solid was filtered, washed with 25 ml heptane and dried (1 hour/90°) to give 8.77 g of solid, which was placed in a medium Ace-Kauffman column over 4 cm alumina and extracted with heptane. Once most of the fluorescent material had been eluted, the pot was cooled to -20°, the solid filtered and dried (1.5 hours/70°) to give 5.52 g (64%) of

yellow 2-methoxy-3-(5-chloro-2-benzoxazolyl)dibenzofuran **6E**, mp 191-193°.

Under nitrogen a mixture of the methoxydibenzofuran **6E** (5.2 g, 14.9 mmoles), lithium iodide (3.48 g, 26.0 mmoles), and 20 ml of collidine was boiled under reflux. The mixture thickened during reflux, necessitating the addition of an additional 40 ml of collidine to aid with stirring. The mixture was cooled somewhat and was poured into 200 ml of 3 *M* hydrochloric acid. An additional 200 ml of water was added and the mixture was stirred at room temperature for 1/2 hour. The resulting solid was collected by filtration, washed with water and dried (16 hours/80°) to give 5.16 g of solid. The solid was placed in a medium Ace-Kauffman column over 4 cm alumina and extracted with heptane. Once all fluorescent material had been eluted, the pot was cooled to room temperature, the solid collected by filtration, and dried (70°/5 hours) to give 3.56 g (71%) of pale yellow needles, mp 244-246°; pmr (200 MHz, saturated at 50°): δ 7.3-7.8 (4H, complex m, H1, H7, H6, H5), 7.63 (1H, dd, *ortho/meta,* $J_{4'-6'}$ = 1.4 Hz, $J_{6'-7'}$ = 8.5 Hz, H6'), 7.71 (1H, dd, *ortho/para,* $J_{4'-7'}$ = 0.7 Hz, H7'), 7.97 (1H, d, *para,* H4'), 7.98 (1H, d, *ortho,* $J_{7-8} \approx 7$ Hz, H8), 8.23 (1H, d, *para,* J_{1-4} <0.5 Hz, H4), 11.43 (1H, sl br s, O*H*).

Anal. Calcd. for $C_{19}H_{10}NO_3Cl$: C, 67.97; H, 3.00; N, 4.17. Found: C, 68.21; H, 3.05; N, 4.12.

9,9-Dipropyl-2-hydroxyfluorene **9**.

Magnesium turnings (10.80 g, 0.444 mole) were heated to 110° for 1 hour under nitrogen. Meanwhile, 2-bromo-9,9-dipropylfluorene (**8**, 133.0 g, 0.404 mole, [19]) was dissolved in 300 ml dry tetrahydrofuran, along with ~0.5 ml of 1,2-dibromoethane entrainer, and ~100 ml of the solution was added to the hot magnesium. The mixture was heated to reflux, and after a short period, formation of the Grignard reagent ensued, resulting in spontaneous boiling. The remainder of the bromide was added at a rate sufficient to maintain reflux. The solution was boiled under reflux for an additional 1 hour after addition was complete, and then cooled to room temperature.

Into a 2-liter round-bottomed flask, equipped with mechanical stirring, pressure equalizing addition funnel, thermometer, and nitrogen inlet, were placed 50.5 ml of trimethyl borate and 250 ml of dry tetrahydrofuran. The solution was cooled to -10° in an acetone/ice bath and the Grignard solution was transferred *via* needle at -10° to -5° with vigorous stirring. The solution was stirred an additional 15 minutes and 34.5 ml of cold glacial acetic acid was added all at once, followed by the dropwise addition of a cold solution of 30% hydrogen peroxide in 40 ml water, keeping the temperature below 0°. The mixture was allowed to warm over a 30 minute period and was washed repeatedly with portions of a saturated solution of ammonium sulfate (1 liter total). The organic layer was washed over magnesium sulfate and concentrated to give a dark oil, which was distilled under vacuum and crystallized from heptane (3-4 ml/g) at -20° to give 30.5 g (28%), mp 116-117°; pmr (60 MHz, 10%): δ = 0.65 (10H, br s, $CH_3CH_2CH_2$), 1.93 (4H, t, $CH_3CH_2CH_2$), 5.08 (1H, s, OH, exchangeable with deuterium oxide), 6.77 (1H, d, H3), 6.84 (1H, s, H1), 7.32 (3H, m, H6, H7, H8), 7.57 (2H, m, H4, H5).

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.51; H, 8.34.

9,9-Dipropyl-2-hydroxy-3-nitrofluorene **11**.

Concentrated (70%) nitric acid was added dropwise over a 15 minute period to a mixture of 200 ml of glacial acetic acid and 2-hydroxy-9,9-dipropylfluorene (**9**, 8.00 g, 30.0 mmoles), keeping the temperature below 30° with the aid of a water bath. The mixture was heated for 1 hour at 80-90°, cooled, and poured into 500 ml of water, forming an emulsion. The mixture was extracted with three 200 ml portions of methylene chloride and the combined organic layers were dried over magnesium sulfate and concentrated. The resulting oil was dissolved in cyclohexane/toluene (8:2) and passed through a 10 cm x 2.5 cm column of Silica Gel with cyclohexane/toluene (8:2) as the eluent. (The small amount of the positional isomer **11A** was abandoned on the column.) The eluate was concentrated; the residual oil dissolved in ethanol (50 ml), and the solution poured into water (250 ml) to precipitate the product as a yellow solid. The solid was collected by filtration, washed with water and dried (2.5 hours/mechanical pump) to give 7.09 g (72%) of yellow nitrophenol, mp 98-101°; pmr (60 MHz, 10%): δ = 0.69 (10H, br s, $CH_3CH_2CH_2$), 1.95 (4H, t, $CH_3CH_2CH_2$), 7.12 (1H, s, H1), 7.32 (3H, m, H6, H7, H8), 7.64 (1H, dd, H5), 8.33 (1H, s, H4), 10.97 (1H, s, OH).

Anal. Calcd. for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.00; H, 6.66; N, 4.55.

3-Amino-9,9-dipropyl-2-hydroxyfluorene **12**.

A mixture of 2.8 g of wet 10% palladium/carbon catalyst and sodium borohydride (8.42 g, 0.223 mole) in 250 ml of ethanol/water (1:1) was treated dropwise over 1 hour with a solution of the nitrophenol **11** (34.8 g, 0.106 mole) dissolved in 150 ml of water, 200 ml of methanol, and 200 ml of ethanol, containing as well sodium hydroxide (40 g, 1.06 moles). The mildly exothermic reaction was kept under 30° with the aid of a cold water bath. The reaction mixture was stirred for an additional hour after addition was complete, and then filtered through polyester cloth to remove the catalyst. The filtrate was diluted by pouring it into 2 liters of water and was neutralized with 6*M* hydrochloric acid to *p*H 6.5-7.0, resulting in the formation of a pink precipitate, which was collected by vacuum filtration and washed with a copious amount of water. After drying (overnight/mechanical pump), 30.5 g (97%) of amine, mp 174-178° dec, was obtained; pmr (60 MHz, 10% in Unisol™): δ = 0.67 (10H, br s, $CH_3CH_2CH_2$), 1.83 (4H, br s, $CH_3CH_2CH_2$), 3.5-8.5 (3H, v br s, NH_2 and OH, exchangeable with deuterium oxide), 6.80 (1H, s, H1), 7.3 (5H, m, H4-H8).

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.07, 81.18; H, 8.20, 8.22; N, 5.07, 5.08.

3-(9,9-Dipropylindeno[3,2-*f*]benzoxazol-2-yl)-2-methoxydibenzofuran (**14**).

A mixture of 3-carboxy-2-methoxydibenzofuran (**1**, 6.98 g, 28.8 mmoles), 50 ml of dry tetrahydrofuran, 2.20 ml (30.2 mmoles) of thionyl chloride, and 0.1 to 0.2 ml of *N*-methylpyrrolidinone under nitrogen was refluxed for 2.5 hours and then allowed to cool to room temperature. The cooled acid chloride was added over several minutes to this solution of 3-amino-9,9-dipropyl-2-hydroxyfluorene (**12**, 8.99 g, 30.2 mmoles), in 50 ml dry tetrahydrofuran and pyridine (4.77 ml, 60.4 moles), resulting in an exotherm and the formation of a precipitate. The mixture was stirred for an additional hour, poured into 400 ml of water, and made acidic to *p*H ~1. The solid was collected by vacuum filtration, washed with water, slurried in 200 ml of methanol, refiltered, and washed with an additional 100 ml of methanol, to give a yellow solid. After drying 10.5 g

(70%) of *N*-(9,9-dipropyl-2-hydroxy-3-fluorenyl)-2-methoxydibenzofuran-3-carboxamide (**13**), mp 252-255° was obtained; ir (potassium bromide, DRC); ν 3305 (NH), 3072 (OH), 2951, 2929, 2869, 2838, 1645 (C=O), 1605 (C=C), 1555 (NH), 1498, 1466, 1450, 1431, 1342 1311, 1276, 1261, 1239, 1219 1187, 1167, 1028 (OCH_3), 891, 860, 842, 818, 743, 699.

Into a 100 ml, 2-necked, round-bottomed flask, equipped with magnetic stirring, nitrogen inlet, thermometer dipping into the solution, and a combination distillation head/air condenser, were placed the amide **13** (10.00 g, 19.2 mmoles), boric acid (0.20 g, 3.2 mmoles) and 40 ml of 2-butoxyethyl ether. The mixture was heated slowly (45 minutes) to reflux (255-260°), held at this temperature for 1/2 hour, and then ~3/4 (30 ml) of the solvent was removed by distillation. The remaining solution was cooled to ~80° and poured into 200 ml of heptane, forming a precipitate. The mixture was stirred to break up the solid and then cooled to -20°. The solid was filtered, washed with 25 ml of heptane and dried (1 hour/90°). The filtrate was concentrated and dried (100°/mechanical pump) to yield an additional 2 g of solid. The combined solids were placed in a medium Ace-Kauffman column over 4 cm of alumina and extracted with heptane. Once most of the fluorescent material had been eluted, the pot was cooled to -20°, the solid filtered and dried (16 hours/80°) to give 7.25 g (75%) of a salmon solid, mp 158-165°, cloudy melt.

The analytical sample was prepared by extraction from alumina with heptane in an Ace-Kauffman column, stopping before material with a yellow fluorescence would have been eluted. The solid obtained from the extract had mp 159-161°.

Anal. Calcd. for $C_{33}H_{29}NO_3$: C, 81.29; H, 6.00; N, 2.87. Found: C, 80.85; H, 6.03; N, 3.01.

3-(9,9-Dipropylindeno[3,2-*f*]benzoxazol-2-yl)-2-hydroxydibenzofuran **15**.

A mixture of the methoxydibenzofuran **14** (6.75 g, 13.4 mmoles), anhydrous lithium iodide (3.16 g, 23.6 mmoles), and 25 ml of collidine was refluxed for 1.5 hours during which time the mixture thickened and then all solids dissolved. The mixture was cooled somewhat and was poured into 250 ml of water and made acidic to *p*H 1-2 with concentrated hydrochloric acid. An additional 200 ml of water was added and the mixture was stirred at room temperature for 1/2 hour. The resulting solid was collected by filtration, washed with water and dried (16 hours/80°). The solid was placed in a medium Ace-Kauffman column over 4 cm alumina and extracted with ethyl acetate. Once all fluorescent material had been eluted, the pot was cooled to room temperature, the solid collected by filtration, washed with 30 ml ethyl acetate and dried (70°/5 hours) to give 5.77 g (88%) of pale yellow 3-(9,9-dipropylindeno[3,2-*f*]benzoxazol-3-yl)-2-hydroxydibenzofuran **15**, mp 304-305°, shrinks 303°; pmr: see Figure 1.

Anal. Calcd. for $C_{32}H_{27}NO_3$: C, 81.16; H, 5.75; N, 2.96. Found: C, 80.69; H, 5.66; N, 2.90.

Dibenzothiophenes.

4-Methoxy-2'-nitrodiphenyl Sulfide **18**.

A solution of sodium carbonate monohydrate (27.4 g, 0.221 mole) in 100 ml of water was prepared, to which was added 4-methoxybenzenethiol (**17**, 25.0 g, 0.179 mole, Aldrich 10,952-5); this dissolved in a few minutes. Then a warm solution of 1-chloro-2-nitrobenzene (**16**, 28.1 g, 0.179 mole, Aldrich 18,576-0) in 125 ml of 95% ethanol was added, and the mixture was heated under reflux for 45 minutes, then at 80° for 20 hours. The heat was removed, and 100 ml of water was added to dissolve salts; the mixture was quenched in 300 ml of water. The solid was filtered, washed with water, slurried in 200 ml of methanol for 5 minutes, filtered, washed with methanol, and dried to give 37.3 g (80%), mp 97-99°.

Anal. Calcd. for $C_{13}H_{11}NO_3S$: C, 59.75; H, 4.24; N, 5.36. Found: C, 59.98; H, 4.43; N, 5.36.

2-Amino-4'-methoxydiphenyl Sulfide **19**.

Into a 3-liter flask were placed 198 g of stannous chloride dihydrate and 264 ml of 12 *M* hydrochloric acid; this was stirred to obtain complete solution, then treated with 38.3 g of 4-methoxy-2'-nitrodiphenyl sulfide (**18**) and 396 ml of acetic acid. A mild exotherm to 67-75° was followed by deliberate heating to reflux at 89° for 20 minutes, by when the mixture became colorless. It was kept overnite at 20°, cooled in ice, and treated with 2.5 l of 6 *M* sodium hydroxide over 3 hours and seeded to obtain the product as a white solid, which was filtered, washed with 500 ml of water, and dried at 50°/30 torr/8 hours to give 37.62 g of crude amine, which was extracted from a large Soxhlet with a mixture of 350 ml of Freon TF and 50 ml of dichloromethane. The extract was cooled to -20° to deposit 31.05 g (92%) of white amine, mp 64.5-66°; pmr (60 MHz, 12%): δ 3.69 (3H, s, CH_3O), 4.23 (2H, br s, all exchanged with deuterium oxide, NH_2), 6.5-6.9 (4H, m, H3, H4, H3', H5'), 6.9-7.5 (4H, m, H5, H6, H2', H6').

Anal. Calcd. for $C_{13}H_{13}NO_3S$: C, 67.50; H, 5.67; N, 6.06. Found: C, 67.32; H, 5.69; N, 6.00.

2-Methoxydibenzothiophene **20**.

The 2-amino-4'-methoxydiphenyl sulfide (**19**) was subjected to diazotization, *etc*, according to the method of Paul Block, Jr., [24] on a related compound to give 7.5% of 2-methoxydibenzothiophene **20**, after recrystallization from a mixture of methanol and *t*-butyl methyl ether at -20°, mp 57.1-58.4° (lit mp 54-55° by a different method [20]); pmr (200 MHz, 6%): δ 3.88 (3H, s, CH_3O), 7.06 (1H, dd, *ortho/meta,* J_{1-3} = 2.5 Hz, J_{3-4} = 8.7 Hz, H3), 7.38 (1H, high-order m, H6), 7.42 (1H, high-order m, H6), 7.59 (1H, d, *meta,* H1), 7.63 (1H, dd, *ortho/para,* J_{1-4} <0.5 Hz, H4), 7.80 (1H, high-order m, H5), 8.06 (1H, high-order m, H8) by COSY.

3-Acetyl-2-methoxydibenzothiophene **21**.

The 2-methoxydibenzothiophene was subjected to a Friedel-Crafts acetylation as described for the corresponding dibenzofuran [16], or for **10** above, to give 55%, mp 163.4-164.9° after recrystallization from a mixture of heptane and toluene; tlc, toluene, showed 1 spot, R_f = 0.26; pmr (200 MHz, 6%): δ 2.68 (3H, s, CH_3CO), 4.00 (3H, s, CH_3O), 7.42 (1H, high-order m, H6), 7.47 (1H, high-order m, H7), 7.57 (1H, s, H1), 7.81 (1H, high-order m, H5), 8.08 (1H, high-order m, H8), 8.18 (1H, s, H4).

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72. Found: C, 70.24; H, 4.79.

2-Hydroxy-3-(6-methyl-2-benzoxazolyl)dibenzothiophene **24**.

In a 150 ml beaker 1.1 g of 3-acetyl-2-methoxydibenzothiophene (**21**) in 25 ml of dioxane was stirred and heated to 55°. A mixture of 12 ml of 10.5% sodium hypochlorite, 12 ml of water, and 4.6 ml of 1 *M* potassium hydroxide was added 1 ml at a time

over 45 minutes, while heating to 57°. A heavy precipitate formed. About 1.2 g of sodium bisulfite was added to obtain a negative potassium iodide/starch paper test, then 6 *M* hydrochloric acid was added to obtain *p*H ≈2, and the mixture was cooled in ice to 5°, and filtered to obtain, after drying, 1.1 g (97%) of white 2-methoxydibenzothiophene-3-carboxylic acid **22**, mp 260-262°.

A mixture of 2-methoxydibenzothiophene-3-carboxylic acid (**22**, 0.97 g, 0.00376 mole), 2-amino-5-methylphenol (**3C**, 0.463 g, 0.00376 mole), 12 ml of 2-butoxyethyl ether, and 0.10 g of boric acid was treated as in the preparation of **4B**. The methylcyclohexane extract was cooled to -20° to obtain **23** as a yellow powder, ≈0.04 g (3%) mp 218-252°, a partially demethylated mixture.

The above mixture was boiled for 1 hour with 5 ml of *sym*-collidine and 0.042 g of lithium iodide, cooled, and filtered to give a solid, mp 276-278°, which was recrystallized from 5 ml of 2-ethoxyethanol, yielding 0.031 g (90%) of **24** as an orange powder, mp 276.5-277.5°.

Anal. Calcd. for $C_{20}H_{13}NO_2S$: C, 72.49; H, 3.95; N, 4.23. Found: C, 72.16; H, 3.89; N, 4.14.

Carbazoles.

3-Methoxy-9-methylcarbazole **26**.

Potassium hydroxide (6.59 g of 85% pellets, 0.100 mole) was dissolved in 200 ml of methanol; to this was added 2-hydroxy-9-methylcarbazole (19.5 g, 0.100 mole, [26]) followed by dimethyl sulfate (11.3 ml, 0.120 mole, MC&B). Following an exotherm to 38° and formation of a heavy precipitate, the mixture was kept at 22°/2 hours and 0°/16 hours, filtered, the solid washed with 1:1 methanol:water, and dried at 50°/30 torr/18 hours to give 15.8 g, mp 93-95°. A second crop of 2.0 g had mp 77-85°. Combined, the dark solids were extracted from a 4 cm column of alumina in a medium Ace-Kauffman column with 300 ml of Freon TF. The liquor was kept at 0°/2 days to give 9.7 g (46%), mp 96.9-98.6° (lit mp 98°, [25]); ir (4.8%): ν 3050 (ArH), 3002 (ArH), 2940 (CH_3N-), 2830 (CH_3O-), 1630 (w), 1605 (w), 1578 (w), 1488 (v s, arom skel), 1473 (v s, arom skel), 1441 (CH_3O-), 1424 (CH_3N-), 1326 (ArN), 1288 (s, ArO), 1258, 1200, 1172 (CH_3O-), 1155 (CH_3N-), 1139, 1121, 1062, 1032 (CH_3O-), 864, 847, 695 (ArH), 642 (w), 632, 610, 538; pmr (200 MHz, 5%): δ 3.7406 (3H, s, C*H*$_3$N), 3.9023 (3H, s, C*H*$_3$O), 7.09 (1H, dd *ortho/meta*, J_{1-2} = 8.8 Hz, J_{2-4} = 2.5 Hz, H2), 7.17 (1H, di-*ortho/meta*, $J_{5-6,6-7}$ = 6.9 Hz, J_{6-8} = 1.2 Hz, H6), 7.25 (1H, dd *ortho/para*, J_{1-4} = 0.5 Hz, H1), 7.31 (1H, ddd *ortho/meta/para*, J_{7-8} = 8.1 Hz, J_{5-8} = 1.1 Hz, H8), 7.43 (1H, di-*ortho/meta*, J_{5-7} = 1.2 Hz, H7), 7.57 (1H, dd, *meta/para*, H4), 8.03 (1H, ddd, *ortho/meta/para*, H5).

3-Acetyl-6-methoxy-9-methylcarbazole **28**.

The 3-methoxy-9-methylcarbazole **26** was subjected to a Friedel-Crafts acetylation as described for the corresponding dibenzofuran [16] to give 29%, mp 140.5-142.5° after recrystallization from a mixture of heptane and toluene, followed by several recrystallizations from 1-butanol to constant melting point; ir (4.6%): ν 3003 (ArH & CH_3CO-), 2938 (CH_3O-), 2835 (CH_3N-), 1663 (s, C=O), 1631, 1597 (s), 1486 (v s, arom skel), 1465 (sh, arom skel), 1438 (CH_3O-), 1428 (CH_3N-), 1365, 1296 (s, ArO), 1269, 1170 (CH_3O-), 1158, 1147, 1128, 1052 (CH_3O-), 1028, 1020, 971, 953, 845, 802, 650, 640, 563; pmr (200 MHz, 5%): δ 2.70 (3H, s, C*H*$_3$CO), 3.79 (3H, s, C*H*$_3$N), 3.93 (3H, s, C*H*$_3$O), 7.13 (1H, dd *ortho/meta*, J_{7-8} = 8.8 Hz, J_{5-7} = 2.5 Hz, H7), 7.25 (1H, dd *ortho/para*, J_{5-8} = 0.6 Hz, H8), 7.30 (1H, dd *ortho/para*, J_{1-2} = 8.7 Hz, J_{1-4} = 0.6 Hz, H1), 7.59 (1H, dd, *meta/para*, H5), 8.07 (1H, dd *ortho/meta*, J_{2-4} = 1.9 Hz, H2), 8.65 (1H, dd, *meta/para*, H4).

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.40; H, 6.06; N, 5.52.

3-Ethyl-6-methoxy-9-methylcarbazole **29**.

The ketone **28** was subjected to a Wolff-Kishner reaction [35] to give about 50% of crude, mp 75-80°. Recrystallization from cyclohexane/heptane at -20° gave 30% as tan granules, mp 89.1-91.5°; ir (4.6%): ν 3003 (ArH), 2963 (C_2H_5), 2932 (CH_3N-), 2900, 2865, 2832 (CH_3O-), 1633 (w), 1610 (w), 1578, 1486 (v s, arom skel), 1440 (CH_3O-), 1427 (CH_3N-), 1341, 1329, 1296 (s, ArO), 1262, 1202, 1155 (CH_3O-), 1249, 1057 (CH_3O-), 1032, 906, 882, 843, 803, 660, 645, 591.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.22; H, 6.82; N, 5.80.

5-Methoxy-2-nitrobiphenyl **31**.

With powerful mechanical stirring for 10 minutes, 5-methoxy-2-nitroaniline (113 g, 0.673 mole, [31]) was treated with 200 ml of 12 *M* hydrochloric acid and 120 ml of water to form a suspension of the paler yellow hydrochloride. The next day a solution of sodium nitrite (46.4 g, 0.673 mole) in 80 ml of water was added under the surface of the suspension during 2 hours at 10-15° at the beginning and 5-10° toward the end, followed by 1 hour of stirring. One liter of benzene was added, followed by a solution of 400 g of sodium acetate trihydrate in 1 L of water at 5-10° during 3 hours, and stirring was continued overnight at 25°, and at 34° for an addtional 24 hours, and then the mixture was heated to 65° and allowed to cool overnight. The benzene layer was filtered (slow), the filtrate washed with 2 x 500 ml of water, dried with 2 successive 100 g portions of potassium carbonate, and evaporated to 168 g of viscous dark oil. The oil was distilled through a heated Claisen, and a main cut bp 156°/0.08-163°/0.12 torr was taken, ≈85 g of colorless oil; tlc (MK6F Silica Gel, *t*-butyl methyl ether, uv) showed 3 spots, the main one of R_f = 0.73 (≈85%); similarly with toluene, main spot R_f = 0.47 (≈85%). The oil in 850 ml of cyclohexane was chromatographed on ≈150 g of Silica Gel (Aldrich 24,217-9), eluting with 1 L of 5% ethyl acetate in cyclohexane, then 1 L of 9% ethyl acetate in cyclohexane to obtain 82.5 g (54%) which showed a single spot on tlc. A small amount was crystallized from methanol at -20°, mp 50.6-51.3° (lit mp 50.6-51.3°, [27]).

3-Methoxycarbazole **32**.

A stirred mixture of ≈82 g of 5-methoxy-2-nitrobiphenyl (**31**) and 265 ml of triethyl phosphite (Aldrich T6-120-4) was boiled under reflux for 24 hours. The phosphite and phosphate esters were distilled under high vacuum. The residue was taken up in 300 ml of 1-propanol, diluted with 300 ml of water, seeded, and kept at 0°, to give 32 g of a sticky orange solid; this was recrystallized from 750 ml of methylcyclohexane at 0° to give 22 g, mp 148-152°; this was extracted from a 4 cm high column of Br. I neutral alumina (Aldrich 19,997-4) with 300 ml of heptane in a medium Ace-Kauffman column to give 18 g (28%) of white carbazole, mp 153.0-155.0° (lit mp 148-149° [27], mp 149-151° [36]); ir (4.8%): ν 3470 (s, NH), 3420, 3060, 3003 (ArH), 2955, 2905, 2835 (CH_3O-), 1630 (w), 1611 (w), 1595 (w), 1491 (v s, arom skel), 1459 (v s, arom skel), 1435 (CH_3O-), 1330, 1320,

1033 (CH_3O-), 1008, 903, 862, 840, 828, 803, 611, 568.

9-Acetyl-3-methoxycarbazole **33**.

A mixture of 17.7 g of 3-methoxycarbazole **32** in 50 ml of dichloromethane was stirred and warmed, then treated with 11.3 ml of acetic anhydride and 2 ml of methanesulfonic acid to give a purple solution, which was boiled under reflux for 1 hour, cooled in ice, and quenched in a solution of 16 g of sodium bicarbonate in 150 ml of water. The organic layer was dried with potassium carbonate and evaporated to 25 g of pale green oil. This was crystallized with great difficulty from 2:5 acetone:ethanol at -20°; the sticky solid was twice recrystallized from the same solvent mixture, once with activated carbon, to give 8.2 g (40%), mp 64-66°; ir (4.6%): ν 3005 (ArH & CH_3CO-), 2959, 2940, 2835 (CH_3O-), 1682 (s, C=O), 1640, 1602, 1588, 1488 (v s, arom skel), 1452 (CH_3O-), 1432, 1371 (s), 1348, 1320 (ArN), 1305 (v s, CH_3CO-), 1290 (s, ArO), 1248, 1195, 1173 (CH_3O-), 1154, 1128, 1036 (CH_3O-), 1009, 981, 862, 842, 605, 580.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.25; H, 5.59; N, 5.83.

2,9-Diacetyl-3-dihydroxycarbazole **35**.

A solution of 9-acetyl-3-methoxycarbazole (11.35 g, 0.0500 mole, **33**) and acetyl chloride (3.91 ml, 4.32 g, 0.0550 mole) in 25 ml dichloromethane was added to a stirred suspension of aluminum chloride (26.7 g, 0.200 mole) in 200 ml of dichloromethane below 6° during 15 minutes, followed by warming to cause reflux for 15 minutes, and cooling in ice to 10°. Cautious addition of 150 ml of 2 *M* hydrochloric acid produced a violent exotherm and the formation of a bright yellow complex, which was decomposed only on warming to reflux. The lower organic layer of 600 ml (from additional dichloromethane used for rinsing) was washed with 50 ml of water, dried with 22 g of potassium carbonate, and evaporated to give 9.5 g of yellow powder, mp 190-194°. This was recrystallized from 300 ml of 1-butanol to give 8.3 g (62%) of long yellow needles; ir (2%): ν 3400-2800 (w, v br, bonded OH), 3125 (w), 3060 (w), 3005 (ArH & CH_3CO-), 1685 (s, CH_3CON), 1640 (v s, CH_3COAr), 1590, 1494, 1455 (arom skel), 1425 (s, arom skel), 1371 (s), 1323 (ArN), 1310 (s, CH_3COAr), 1268, 1243, 1228 (v s, ArO), 1211, 1200, 1156 (w), 1147 (w), 1122 (w), 1063 (w), 1038 (w), 1023, 987 (w), 970, 943, 862; pmr (200 MHz, 5%): δ 2.69 (3H, s, CH_3COC), 2.82 (3H, s, CH_3CON), 7.33 (1H, s, H4), 7.36 (1H, td, di-*ortho/meta*, J_{5-6} = 7.6 Hz, J_{6-7} = 7.5 Hz, J_{6-8} = 0.9 Hz, H6), 7.52 (1H, td, di-*ortho/meta*, J_{5-7} = 1.4 Hz, H7), 7.80 (1H, dt *ortho/meta/para*, J_{7-8} = 8.5 Hz, J_{5-8} = 0.6 Hz, H8), 7.90 (1H, ddd, *ortho/meta/para*, H5), 8.85 (1H, s, H1), 12.32 (1H, s, O*H*).

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.84; H, 4.83; N, 5.23.

3'-Methoxyacetanilide **37**.

Under nitrogen with stirring in a water bath m-anisidine (195 g, 1.585 moles, Lancaster 3806, **36**) was treated with acetic anhydride (168 ml, 178 g, 1.74 moles, Fisher A-10-4) dropwise below 100° during 15 minutes. The bath was heated to boiling for 1 hour, heating stopped, 100 ml of water added, and the hot liquid transferred to a beaker, to which 200 ml of methanol and 350 ml of water were added, followed by seeding and prolonged cooling at -2° to give a solid, which was washed on the filter with 500 ml of pre-cooled 1:1 methanol:water and dried at 50°/20 torr/22 hours to give 226 g (86%), mp 82-83.5° (lit mp 80-81° [37]).

5'-Methoxy-2'-nitroacetanilide **38**.

Nitration of 3'-methoxyacetanilide **37** was carried out as described [31] to give an isomer mixture, mp 115-127°. This was extracted from a 2 cm high column of Silica Gel in an Ace-Kauffman column with methylcyclohexane, and the extract kept at 22° to give 46%, mp 128.5-129.5° (lit mp 121-123° [31], 129-131° [38]; ir (6.8%): ν 3340 (bonded NH *trans*), 3135 (w, bonded NH *cis*), 3010 (ArH), 2975 (w), 2943 (w), 2840 (CH_3O-), 1697 (s, C=O), 1608 (s, arom skel), 1590 (v s, arom skel), 1541 amide II), 1491 (s, NO_2), 1451 (s, CH_3O-), 1424 (s, CH_3CO-), 1370, 1318 (s, NO_2), 1277 (v s, ArO), 1240, 1210 (s), 1174, 1163, 1087 (CH_3O-), 1032, 1010, 961 (w), 952 (w), 878, 862, 851, 822, 688, 661, 638, 620, 585, 520; pmr (60 MHz, 8%): δ 2.32 (3H, s, CH_3CO), 4.01 (3H, s, CH_3O), 8.45 (1H, s, H6'), 8.53 (1H, s, H3'), 10.71 (1H, br s, N*H*).

Further extraction of the column with toluene gave 20% of 3'-methoxy-4'-nitroacetanilide, mp 167-169°.

4'-Bromo-5'-methoxy-2'-nitroacetanilide **39**.

A solution of 5'-methoxy-2'-nitroacetanilide (21.0 g, 0.100 mole, **38**) and sodium acetate (8.37 g, 0.102 mole) in 125 ml of acetic acid was heated with stirring to 55°. Then bromine (16.16 g, 5.2 ml, 0.101 mole) was added during about 15 minutes at 55°, followed by 30 minutes at this temperature. The nearly colorless mixture was quenched in 400 ml of water containing 1 g of sodium bisulfite. Yellow needles of **39** were collected on a filter, washed with 500 ml of water, and dried, to obtain 25.8 g, mp 127.5-133.5°. This was recrystallized from 250 ml of toluene to give 18.0 g (62%), mp 139-140.5°; ir (2.6% in chloroform): ν 3341 (NH), 3128 (w), 3015 (ArH & CH_3CO-), 1702 (C=O), 1602 (arom skel), 1582 (arom skel), 1535 (amide II), 1488 (NO_2), 1467, 1451 (CH_3O), 1405, 1370, 1330 (NO_2), 1308, 1271 (v s, ArO), 1245, 1205 (ArO), 1103, 1053 (CH_3O), 1010, 902, 862 (CNO_2), 662; pmr (60 MHz, 8% in deuteriochloroform): δ 2.29 (s, 3H, CH_3CO); 4.00 (s, 3H, CH_3O); 8.41 (s, 1H, H6); 8.65 (s, 1H, H3); 10.71 ppm (br s, 1H, N*H*).

Anal. Calcd. for $C_9H_9BrN_2O_4$: C, 37.52; H, 2.80; N, 9.72; Br, 27.74. Found: C, 37.77; H, 2.91; N, 9.80; Br, 27.69.

4-Bromo-5-methoxy-2-nitroaniline **40**.

Hydrolysis of the amide was accomplished by boiling it (17.6 g, 0.069 mole, **39**) under reflux with a mixture of 75 ml of 12 *M* hydrochloric acid and 15 ml of acetic acid for 1 hour, during which time 4-bromo-5-methoxy-2-nitroanilinium chloride separated as flakes. After addition of 125 ml of water, the solid was filtered and dried to give the free base as tiny yellow needles, mp 175.5-178.5°, 14.0 g (93%); ir (2.6%): ν 3512 (NH_2), 3388 (NH_2), 3015 (w, ArH), 2975 (w), 2940 (w), 2842 (CH_3O), 1618 (s, NH_2), 1582 (C=C), 1568, 1560, 1490 (NO_2), 1460, 1445 (CH_3O-, 1372, 1315, 1364 (v s, NO_2), 1118, 1042 (CH_3O), 900, 850, 818, 618 (w), 578 (w); pmr (60 MHz, 4.5% in Unisol-d): δ 3.95 (s, 3H, CH_3O); 6.53 (s, 1H, H6); 6.99 (br s, 2H, NH_2); 8.24 (s, 1H, H3).

Anal. Calcd. for $C_7H_7BrN_2O_3$: C, 34.03; H, 2.86; N, 11.34; Br, 32.34. Found: C, 34.14; H, 2.84; N, 11.38; Br, 33.19.

4-Bromo-5-methoxy-2-nitrobiphenyl **41**.

A mixture of 4-bromo-5-methoxy-2-nitroaniline (98.6 g, 0.400 mole, **40**), 70 ml of water, 120 ml of 12 *M* hydrochloric

0.400 mole, **40**), 70 ml of water, 120 ml of 12 *M* hydrochloric acid, and 1000 ml of benzene was stirred rapidly and treated with a solution of sodium nitrite (27.6 g, 0.400 mole) in 50 ml of water at 18-10° during about 1 hour. Since some tan solid remained, more sodium nitrite was added so that nearly all solid dissolved. Rapid stirring at 26° for 20 hours was followed by a similar period at 40°. The mixture was cooled in ice to 10°, filtered from a little solid, the filtrate separated, and the organic layer was washed with 800 ml, then 300 ml of 10% sodium chloride, dried over potassium carbonate, and evaporated to obtain 108 g of dark oil; this was distilled through a heated Claisen until decomposition in the pot began. An orange oil was obtained, bp 198°/1.3 torr-165°/0.8 torr, 75 g (61% crude), which was used without further purification.

For assays, some material that crystallized on keeping and scratching was recrystallized from ethanol to give tan spars, mp 90-91°; ir (5.5% in chloroform): 3010 (ArH), 2775 (CH_3), 2943 (CH_3), 2853 (CH_3), 1593 (arom skel), 1563 (s, arom skel), 1518 (s, arom skel), 1480 (s, NO_2), 1462, 1442 (CH_3O), 1380, 1342 (v s, NO_2), 1282 (ArO), 1248, 1210, 1114, 1062, 1036 (CH_3O), 1018, 896, 860, 839, 698 (ArH), 665, 632 (w).

Anal. Calcd. for $C_{13}H_{10}BrNO_3$: C, 50.67; H, 3.27; N, 4.55; Br, 25.93. Found: C, 50.99; H, 3.38; N, 4.53; Br, 25.89.

2-Bromo-3-methoxycarbazole **42**.

The biphenyl (75 g, 0.243 mole, **41**) was boiled under reflux with 200 ml of triethyl phosphite for 19 hours under argon. The excess triethyl phosphite and by-product triethyl phosphate were removed by distillation at 0.8 torr. The residue was taken up in 200 ml of 1-propanol, diluted with 50 ml of water, scratched to initiate crystallization, and the mixture was cooled to 5°. The carbazole was filtered and washed with methanol to give, after drying, 14.8 g of tan solid, mp 187-192°. This was extracted from 3 cm of alumina (Aldrich 19,997-4) in a medium Ace-Kauffman column with a mixture of 300 ml of heptane and 30 ml of toluene. The extract was cooled in ice, filtered, washed with hexane, and dried to give 13.6 g (20%) of white solid, mp 193-195.5°; ir (1% in chloroform): ν 3470 (NH), 3065 (w), 3010 (ArH), 2960 (CH_3), 2940 (CH_3), 2840 (CH_3O-), 1605 (NH), 1493 (arom skel), 1472 (arom skel), 1462 (v s, arom skel), 1449 (arom skel), 1431 (CH_3O-), 1313, 1301 (s, ArO), 1257, 1201, 1175 (ArO), 1152, 1113, 1045 (CH_3O), 1025, 1012, 930, 853, 835, 713, 662, 621, 570 (w).

Anal. Calcd. for $C_{13}H_{10}BrNO$: C, 56.55; H, 3.65; N, 5.07; Br, 28.94. Found: C, 56.75; H, 3.77; N, 5.11; Br, 29.17.

2-Bromo-9-ethyl-3-methoxycarbazole **43**.

The 2-bromo-3-methoxycarbazole (13.32 g, 0.0482 mole, **42**) was added in portions to sodium hydride (2.02 g of 60% in oil, 0.0506 mole, previously washed with ether) under 70 ml of dry *N,N*-dimethylformamide below 17° in an ice bath. When evolution of hydrogen ceased, ethyl iodide (4.2 ml, 0.053 mole) was added dropwise at 9-11°. An exothem to 24° was followed by deliberate heating to 50°. The solvent was evaporated, and the residue was partitioned between 100 ml of *t*-butyl methyl ether and 50 ml of water. The organic layer was filtered thru Whatman 1PS paper and evaporated to yield 13.7 g (93% crude) of pale oily product, which was used without further purification.

The analytical sample was obtained by recrystallization from 2-propanol/acetone, then ethanol, mp 85.5-87.5 as white needlets; ir (5% in chloroform): ν 3055, (ArH), 3005 (ArH), 2977 (C_2H_5), 2938 (CH_3), 2895 (C_2H_5), 2840 (CH_3O), 1599 (arom CN), 1486 (arom skel), 1470 (v s, arom skel), 1462 (v s, arom skel), 1431 (CH_3O-), 1421 (C_2H_5), 1381, 1349, 1336, 1310 (s, ArO), 1286, 1254, 1200, 1178, 1156 (ArO), 1129, 1089, 1052, 1045 (CH_3O), 1023, 1012, 945 (w), 913 (w), 869, 849, 701, 662 (w), 581 (w); pmr (200 MHz, 2%): δ 1.39 (3H, t, $J_{1'-2'}$ = 7.3 Hz, CH_3CH_2-), 4.00 (3H, s, CH_3O), 4.27 (2H, q, CH_3CH_2-), 7.20 (1H, td, di-*ortho/meta*, J_{5-6} = 7.8 Hz, J_{6-7} = 7.1 Hz, J_{6-8} = 1.2 Hz, H6), 7.36 (1H, ddd *ortho/meta/para*, J_{7-8} = 8.3 Hz, J_{5-8} = 0.7 Hz, H8), 7.47 (1H, td, di-*ortho/meta*, J_{5-7} = 1.3 Hz, H7), 7.58 (1H, s, H1 or H4), 7.59 (1H, s, H1 or H4), 7.90 (1H, ddd, *ortho/meta/para*, H5).

Anal. Calcd. for $C_{15}H_{14}BrNO$: C, 59.23; H, 4.64; N, 4.60; Br, 26.27. Found: C, 59.37; H, 4.77; N, 4.63; Br, 26.62.

2-Cyano-9-ethyl-3-methoxycarbazole **44**.

The 2-bromo-9-ethyl-3-methoxycarbazole (13.0 g, 0.0428 mole, **43**) and copper(I) cyanide (4.60 g, 0.0513 mole) in 15 ml of *N,N*-dimethylformamide were boiled under reflux for 19 hours with powerful magnetic stirring. All dissolved within 40 minutes. When cooled to ≈60° the mixture was treated with a solution of 10.5 g of potassium cyanide in 35 ml of water, and stirred 1 hour. The solid was filtered, the lumps being broken up, washed on the Büchner with 250 ml of water, and dried to give 11.0 g of crude, mp 145-155°. This was extracted from a Soxhlet overnight with 250 ml of heptane, and the extract was cooled in ice to give 9.70 g (91%), mp 148-155.5°. The tlc on MK6F Silca Gel, *t*-butyl methyl ether, uv, showed 5-10% of a non-fluorescent impurity at R_f = 0.65 and 90-95% ArCN with a blue fluorescence at R_f = 0.69. This material was used in the next reaction.

The analytical sample was prepared by means of two recrystallizations from 1-propanol to give huge prisms, mp 158-160°; ir (4% in chloroform): ν 3060 (ArH), 3010 (ArH), 2980 (C_2H_5), 2940 (CH_3), 2890 (C_2H_5), 2840 (CH_3O), 2224 (CN), 1630 (arom CN), 1567, 1560 (sh), 1492 (arom skel), 1475 (v s, arom skel), 1464 (arom skel), 1434 (s, CH_3O), 1382 (w), 1351, 1324 (s, ArO), 1256, 1202, 1178, 1158 (ArO), 1088, 1061, 1028 (CH_3O), 1017 (sh), 861, 715, 660 (ww), 597 (w).

Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.86; H, 5.60; N, 11.26.

9-Ethyl-3-methoxycarbazole-2-carboxylic Acid **45**.

A solution of 85% potassium hydroxide pellets (9.89 g, 0.150 mole) in 120 ml of water was prepared with stirring. Then the above nitrile (9.40 g, 0.0375 mole, **44**) and 150 ml of glycol were added. Solvent was distilled to obtain a reaction temperature of 135°, and the mixture was boiled under reflux for 24 hours, then cooled to 25°. The almost clear solution was filtered, and the filtrate was made acid with 30 ml of 6 *M* hydrochloric acid. The resulting gum was stirred mechanically for 40 minutes, filtered, washed with water, then 50% methanol, and dried to give 9.29 g, mp 158-160.5°. This was recrystallized from 70 ml of xylenes at 0° to give 7.74 g (76%), mp 158.5-160.5°; when mixed with the nitrile, mp 130-147°. A second crop of 0.78 g (8%) of lower quality was obtained on cooling filtrates to -20°.

The analytical sample was prepared by recrystallization from 20 ml/g of 1-butanol, mp 162-163°; ir (4% in chloroform): ν 3260 (br, OH), 3010 (ArH), 2980 (C_2H_5), 2945 (CH_3), 2848 (w, CH_3O), 1722 (v s, C=O), 1631 (arom CN), 1474 (vs, arom skel), 1462 (arom skel), 1439 (CH_3O), 1382, 1356, 1329, 1245, 1208, 1161, 1157 (ArO), 1131 (w), 1098, 1059, 1022 (CH_3O), 1015

(sh), 930 (w), 690, 662, 630 (w), 641, 583 (w).

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.35; H, 5.65; N, 5.21.

9-Ethyl-3-hydroxy-2-(6-methyl-2-benzoxazolyl)carbazole **47**.

A mixture of the above acid (1.87 g, 0.00695 mole, **45**), 6-amino-*m*-cresol (0.856 g, 0.00695 mole, Lancaster 6565, **3C**), 0.08 g of boric acid, and 12 ml of 2-butoxyethyl ether was heated with stirring under argon under a T-head so that the water formed distilled out, then under reflux at 256° for 1 hour. A total of 7 ml of solvent distilled. At 25° the mixture was quenched in 20 ml of methanol, cooled to -20° when some crystals appeared, then to -65°; the suspension was filtered and dried to give 0.25 g of yellow solid, mp 178-190°, a mixture of 9-ethyl-3-methoxy-2-(6-methyl-2-benzoxazolyl)carbazole **46** and the 3-hydroxy-**47**. The filtrates were diluted to 50 ml with methanol and kept at -20° overnite for a second crop of 0.17 g, total 0.42 g (17% crude). This mixture was used in the next step.

The above mixture of ArOMe and ArOH (0.42 g, ≈0.0012 mole) and lithium iodide (0.30 g, 0.0022 mole) in 5 ml of 2,4,6-collidine was boiled under reflux, with stirring and argon, for 1 hour; brought down to ≈40°, and quenched in 25 ml of 3 *M* hydrochloric acid. This was filtered and dried to give 0.41 g of crude **47**, which was extracted from 3 cm of alumina (Aldrich 19,997-4) with 30 ml of ethyl acetate in a small Ace-Kauffman column. The clear, dark orange extract was kept at -65° to give 0.262 g (66%) of pure product, mp 195-197.5°; pmr (200 MHz, 3%): δ 1.45, (3H, t, $J_{1''\text{-}2''}$ = 7.2 Hz, CH_3CH_2), 2.50 (3H, s, CH_3Ar), 4.33 (2H, q, CH_3CH_2-), 7.15 (1H, dd, *ortho/meta*, $J_{4'\text{-}5'}$ = 8.1 Hz, $J_{5'\text{-}7'}$ = 1.8 Hz, H5'), 7.17 (1H, td, di-*ortho/meta*, $J_{5\text{-}6}$ = 7.8 Hz, $J_{6\text{-}7}$ = 7.0 Hz, $J_{6\text{-}8}$ = 1.0 Hz, H6), 7.31 (1H, ddd *ortho/meta/para*, $J_{7\text{-}8}$ = 8.3 Hz, $J_{5\text{-}8}$ = 0.7 Hz, H8), 7.38 (1H, dd, $J_{4'\text{-}7'}$ <0.5 Hz, H7'), 7.46 (1H, td, di-*ortho/meta*, $J_{5\text{-}7}$ = 1.2 Hz, H7), 7.56 (1H, dd, *ortho/para*, H4'), 7.73 (1H, d, *para*, $J_{1\text{-}4}$ = 0.6 Hz, H4), 7.90 (1H, d, *para*, H1), 8.03 (1H, ddd, *ortho/meta/para*, H5), 11.22 (1H, s, O*H*), by COSY.

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.54; H, 5.36; N, 7.91.

2-(9,9-Dipropylindeno[3,2-*f*]-2-benzoxazolyl)-9-ethyl-3-hydroxycarbazole **49**.

Condensation of 9-ethyl-3-methoxycarbazole-2-carboxylic acid **45** with 3-amino-9,9-dipropyl-2-hydroxyfluorene **12** was carried out as described above to give, after dilution of the cooled mixture with methanol and storing it at -20°, a yellow solid in 25% crude yield, mp 245-265°. Tlc with *t*-butyl methyl ether, showed ≈40% of ArOMe **48** with a blue fluorescence under long-wave ultraviolet excitation at R_f = 0.73, and ≈60% ArOH **49** with a pink-orange fluorescence at R_f = 0.80. This mixture was used in the next step.

The above mixture (0.48 g, 0.906 mmole) and lithium iodide (0.24 g, 1.800 mmoles) was boiled under reflux in 5 ml of 2,4,6-collidine with stirring under argon for 1 hour, cooled to ≈40° and quenched in 25 ml of 3 *M* hydrochloric acid. The precipitated solid was washed with methanol and dried to give 0.44 g (94% crude), which was extracted as above to give, on cooling to 25°, 0.060 g (13%) of huge orange spars, mp 278.5-280.5°; this was used for assays and electronic spectra. A second crop at -20°, mp 276.5-277.5°, 0.240 g (51%, total 64%) was obtained; pmr (200 MHz, 3%): δ 0.68 (10H, br s, $CH_3CH_2CH_2$), 1.46 (3H, t, $J_{1'\text{-}2'}$ = 7.0 Hz, CH_3CH_2N-), 2.03 (4H, t, $J_{1'''\text{-}2'''}$ = 7.0 Hz, $CH_3CH_2CH_2$), 4.36 (2H, q, CH_3CH_2N-), 7.19 (1H, td, di-*ortho/meta*, $J_{5\text{-}6}$ = 7.8 Hz, $J_{6\text{-}7}$ = 7.0 Hz, $J_{6\text{-}8}$ = 1.1 Hz, H6), 7.31-4.41 (3H, complex m, H6', H7', H8'), 7.49 (1H, ddd *ortho/meta/para*, $J_{7\text{-}8}$ = 8.2 Hz, $J_{5\text{-}8}$ = 0.8 Hz, H8), 7.47 (1H, td, di-*ortho/meta*, $J_{5\text{-}7}$ = 1.2 Hz, H7), 7.60 (1H, d, *para*, $J_{4'\text{-}10'}$ = 0.7 Hz, H10'), 7.75 (1H, cm, H5'), 7.79 (1H, d, *para*, $J_{1\text{-}4}$ = 0.6 Hz, H4), 7.966 (1H, d, *para*, H4'), 7.974 (1H, d, *para*, H1), 8.07 (1H, ddd, *ortho/meta/para*, H5), 11.26 (1H, s, O*H*), by COS.

Anal. Calcd. for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.60. Found: C, 80.95; H, 6.28; N, 5.66.

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