Syntheses and Photophysical Properties of Fluorescent 2-Aryl-3-hydroxy-4-chromenones

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The particle detectors proposed for the Super-conducting Super Collider contain polystyrene scintillation fibers as a component. Scintillation fluors soluble in styrene are required which have improved light output and response time. New 2-aryl-3-hydroxy-4-chromenones related to 3-hydroxyflavone were prepared which displayed these improved properties. Improved solvent systems for chromenone formation were essential in the synthesis of two of the chromenones. One chromenone produced fluorescence emission at 560 nm with a quantum yield of 0.53 and a scintillation decay time of 5 nsec.

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Introduction.

Major parts of the particle detectors envisioned for the Super-conducting Super Collider (SSC) are to be fabricated from bundles of scintillating polystyrene fibers several meters long [1-3]. The scintillation fluor or the shifter, if a primary fluor is to be used, must have a number of properties that were not available in any fluor when this work was begun [4]. Among these properties are fluorescence emission at 550-600 nm, fluorescence quantum yield (Φ) ≥ 0.4 (preferably 1.0), scintillation decay time (τ) of ≤ 5 nsec (preferably 2.0 nsec), and extreme thermal, chemical, photochemical, and radiolytic stability, as well as sufficient solubility in both styrene and polystyrene [5]. Transparency of the fluor to its own emission wavelengths is a crucial property, a requirement now believed to be obtainable only from an organic molecule which displays excited-state intramolecular proton-transfer (ESIPT) fluorescence.

For several years the benchmark compound has been the ESIPT fluor 3-hydroxyflavone (3HF, **5** with R = H and Ar = C_6H_5 in Scheme 1, [6]) which has, in toluene, an emission peak at 530 nm (too short), with $\Phi \approx 0.3$ (too low), and $\tau = 8.8$ nsec (much too slow). It is too reactive chemically and not sufficiently soluble in polystyrene ($\approx$1% w/w) to be used as a sole fluor.

A number of 3-hydroxyflavone derivatives with simple substituents on the 2-phenyl group have been prepared [7-8] of which one of the most effective, 2-(4'-biphenylyl)-3-hydroxy-4-chromenone (**5e**), which we also prepared, had emission at 544 nm (possibly acceptable), $\Phi = 0.5$ (acceptable), but had $\tau = 8$ nsec (still too slow) as well as limited solubility (Table 1). The hypothesized electron movement for the S_0 - S_1 transition in 3HF [4] shows that a 2-aryl substituent with a low enough energy barrier to undergo this transition, which requires coplanarity of the 2-aryl group with the chromenone moiety, could raise the extinction coefficient (ε) significantly, if it provides a sufficiently extended π-electron system. A recent examination of the relationship of ε and τ by Paul Cahill confirmed an inverse relationship [9]; thus one of the major attributes to be sought is high ε. Cahill also found a linear relationship between τ and the emission wavelength (λ em); thus there is no theoretical reason why even a red-emitting fluor of high Φ cannot have $\tau < 5$ nsec.

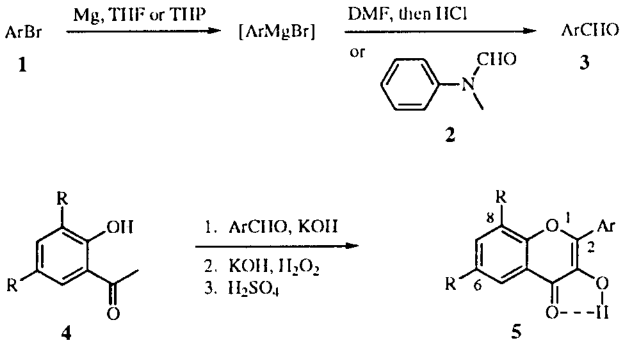
In this work we describe the syntheses of some new 3-hydroxyflavones which display improved properties compared with 3HF in terms of Φ, ε, τ and λ em while retaining adequate solubility.

Discussion and Results.

Syntheses (See Scheme 1).

Scheme 1

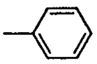
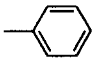
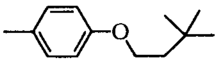
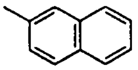
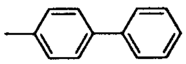
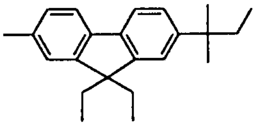
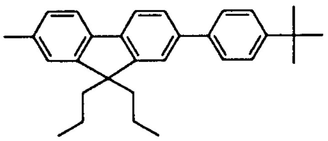
Synthesis of 3-Hydroxyflavones



Aldehydes needed as intermediates for flavones **5a**, **5b**, **5d**, and **5e** were obtained commercially. The aldehyde **3c** needed for 4-chromenone **5c** was prepared by a Williamson ether synthesis from 4-hydroxybenzaldehyde and 1-bromo-3,3-dimethylbutane. Aldehyde **3f** was obtained in 78% yield by reaction of the Grignard reagent from bromoarene **1f** with *N*-methyl-*N*-(2-pyridyl)-formamide [10]. Aldehyde **3g** was obtained impure in only 12% yield by this method, but was obtained in 78% yield by reaction of the Grignard reagent from bromoarene **1g** with *N,N*-dimethylformamide followed by hydrolysis with hydrochloric acid [11].

The flavones were prepared by Pla-Dalmau's modification [7-8] of Smith's method [12] which makes use of a much larger amount of 30% hydrogen peroxide. Flavones **5a-5e** were prepared in adequate to good yield by this modification, which utilizes an initial solvent mixture of 1:4 water:ethanol by volume. Aldehydes **3f-3g** would not dissolve in this mixture, so 1:4:8 water:ethanol:tetrahydrofuran was used in the initial reaction mixture, which becomes biphasic. Flavone **5f** could not be obtained pure, and flavone **5g**, while obtained pure, appeared in only 11% yield. Clearly the dianion intermediate from 2'-hydroxyacetophenone, which is both a phenoxide and an enolate, will not dissolve in sufficient concentration in the non-protic solvent layer in which most of the aldehyde is to be found. In fact, in one run, aldehyde **3g** was recovered intact from the whole process when tetrahydrofuran and ethanol were used. It was then found that the potassium hydroxide would dissolve in absolute ethanol and the organic intermediates would dissolve in dioxane and these two solutions formed a single phase reaction mixture; this modification gave pure flavone **5f** in 6% yield and raised the yield of pure flavone **5g** to 23%.

Table 1
Selected Properties of 2-Aryl-3-hydroxy-4-chromenones **5**

No.	R	2-Aryl Group	λ max	ε	λ fl em	Φ [b]	Soly. [d]
5a	H		354 nm 340 304 237	17,000 21,000 15,000 23,000	528 nm [a]	0.27 [c] 0.25	5.2 g/l or 0.026 *M*
5b	CH_3		357 342 313 247 238 206	15,000 17,000 16,000 22,000 19.000 18,000	522 [a]	0.26	2.6 g/l or 0.011 *M*
5c	H		370 (sh) [b] 356 319	17,000 19,000 9,000	531 [b]	0.25	53 g/l or 0.18 *M*
5d	H		369 351 314 272 244 215	23,000 29,000 16,000 12,000 41,000 35,000	542 [a]	0.43	1.2 g/l or 0.0048 *M*
5e	H		365 (sh) 352 318 257 232 207	— 30,000 18,000 16,000 19,000 29,000	544 [b]	0.49	0.54 g/l or 0.0017 *M*
5f	H		388 (sh) [b] 371	32,000 38,000	545 [b]	0.50	>100 g/l or >0.22 *M*
5g	H		395 (sh) [b] 377	44,000 52,000	560 [b]	0.53	10 g/l or 0.020 *M*

[a] Uncorrected in cyclohexane on Perkin-Elmer LS-5B. [b] In toluene. [c] Deterenined on Perkin-Elmer MPF-44A. [d] In xylenes at 20°.

Solubility (See Table 1).

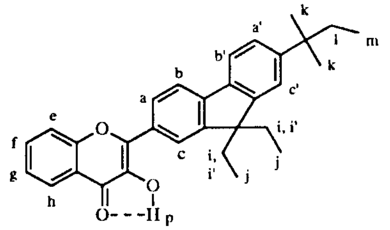
Mixed xylenes were used to simulate the solvent properties of polystyrene. We found that a 0.5% solution of 3HF (0.026 *M*) was obtainable in xylenes at 20° compared with an ≈ 1% solution obtainable in hot styrene monomer; the ≈ 1 % of 3HF is compatible with polystyrene for long time periods [13]. We tried to prepare 8-

t-butyl-3-hydroxy-6-methylflavone to obtain better solubility and possibly to protect the chromenone from reaction with oxygen, which is one of the reported modes of degradation of 3HF [14]. The *t*-butyl group in 2-*t*-butyl-4-methylphenyl acetate was not compatible with the Fries rearrangement [15]. No such problem was encountered with 2,4-dimethylphenyl acetate in the preparation of flavone **5b**. Surprisingly, the molar solubility of **5b** was only 42% of that of 3HF (**5a**), thus **5b** would not have been useful as a sole fluor; besides, no other properties were improved. Chromenone **5c** was prepared originally to obtain better solubility than that of 3HF in polysiloxanes [16-17]. It proved to have 7 times the molar solubility of 3HF in xylenes. The 2-naphthyl (**5d**) and 4-biphenylyl (**5e**) derivatives had only about 1/5 and 1/15 the molar solubility of 3HF, while the fluorenyl derivative **5f** had >8.5 times the molar solubility of 3HF and >120 times the molar solubility of the related **5e**. The largest flavone **5g** was comparable with 3HF in molar solubility, and soluble enough to be used as a shifter. Clearly the alkane groups in **5f** and **5g** more than compensate for the rigidity of their aromatic moieties.

Photophysical Properties (See Table 1).

Table 3

Interpretation of PMR Spectrum of 2-Aryl-3-hydroxy-4-chromenone **5f** (Varian XL 200 MHz)

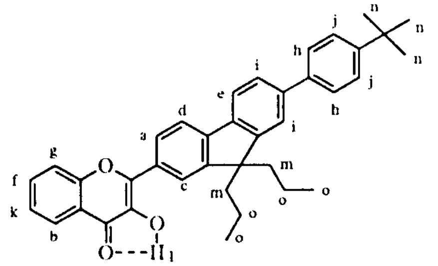


H	δ (ppm)	#Hs	Multiplicity	J = (Hz)
a	8.278	1	dd	ab = 8.1, ac = 1.7
b	7.816	1	d	bc = 0.6
c	8.227	1	d	-
a'	7.345 [a]	1	dd	a'b' = 7.9, a'c'= 1.7
b'	7.699	1	d	b'c' = 0.7
c'	7.310 [a]	1	d	-
e	7.647	1	ddd	ef = 8.5, eg = 1.7, eh = 0.7
f	7.720 [b]	1	dd	fg = 6.5, fh = 1.6
g	7.423 [b]	1	ddd	gh = 8.1
h	8.270	1	ddd	-
i	2.145 [c]	2	dd	i,i' = 6.8, i,j = 7.6
i'	2.077 [c]	2	dd	i',j = 7.3
j	0.377	6	dd	-
k	1.359	6	s	-
l	1.697	2	q	l,m = 7.4
m	0.692	3	t	-
p	7.091 [d]	1	s	-

[a] Protons a' and c' pick up ≈ 17% enhancement when proton k is saturated during one-dimensional NOE difference spectroscopy. This shows which ring of the fluorene contains these protons. [b] Decoupling proton h disturbs an ortho coupling to g and a meta coupling to f. This and COSY established e, f, g and h. [c] Decoupling j resulted in an AB pattern for i and i'. [d] Saturation of the small water peak at 1.6 ppm depleted proton p by ≈ 38% by exchange.

Table 2

Interpretation of PMR Spectrum of 2-Aryl-3-hydroxy-4-chromenone **5g** (Varian XL 200 MHz)



H	δ (ppm)	#Hs	Multiplicity	J (Hz)
a	8.295	1	dd	ad = 8.4, ac = 1.6
b	8.272 (COSY)	1	[a]	bf = 1.5, bg = 0.7, bk = 6.5
c	8.260	1	[a]	cd = 0.7
d	7.853	1	dd	
e	7.812	1	d	ei = 8.3
f	7.727	1	ddd	fg = 6.3, fk = 8.5
g	7.649 (COSY)	1	[a]	
h	7.629	2	[b]	jh = 8.3
i	7.585-7.636	2	[a]	
j	7.510	2	[b]	
l	7.122	1	s, v br	
m	2.070-2.165	4	m	
n	1.390	9	s	
o	0.653-0.831	10	m	

[a] Covered by other multiplets. [b] A *para* pattern.

Compared with 3HF (**5a**) the substitution pattern in 6,8-dimethyl-3-hydroxyflavone (**5b**) reduced the extinction coefficient of the important long-wave absorption bands, and caused a hypsochromic shift of 6 nm in the fluorescence emission. These were not desirable effects for our application because of the reduced light transmission of polystyrene at wavelengths shorter than 570 nm [18]. The 2-(2-naphthyl)chromenone **5d** and the 2-(4-biphenylyl)chromenone **5e** had useful increases in ε, desirable bathochromic shifts of emission to ≈ 543 nm, and increased Φ, but scintillation decay times remained slow, ≈ 8 nsec for **5e**, compared with ≈ 9 nsec for 3HF, despite a 50% increase in ε. Surprisingly, the new chromenone **5g** was much faster, τ = 5 nsec as a shifter; the details will be reported elsewhere. With Φ = 0.53, higher than that of any other chromenone with ESIPT fluorescence we know of, **5g** had higher effective light output in polystyrene than any of the other flavones tested, and the fluorescence peak occurred at the desirably bathochromically shifted wavelength of 560 nm. The new flavone **5f** showed an ε (38,000) intermediate between those of **5e** (30,000) and **5g** (52,000), and about the same emission peak wavelength as that of **5e** (544 nm).

These photophysical relationships between **5e**, **5f**, and **5g** resemble those found for a series of oligophenylene laser dyes containing bridged oligophenylenes with *t*-alkyl auxofluors [19]. The fluorene **5f** is clearly a better light absorber than the biphenyl **5e**. The additional phenyl group in **5g** is clearly utilized in the S_0 - S_1 transition as shown by the 37% increase in ε over that of **5f**, as well as bathochromic shifts in absorption (6 nm) and in fluorescence (15 nm), indicating that all aromatic rings participate and are coplanar in the excited state. Calculations using the ZINDO program on the CAChe Scientific system gave a good match of absorption and emission with the experimental values for 3HF [9], but gave a poor match of the absorption maximum λ with that of **5g**, indicating erroneously that the fluorene group and the chromenone group were perpendicular in the ground state [20]. The calculated λ em of 540 nm was in fair agreement with the actual value of 560 nm. Intuitive modification and synthesis of new structures is still an important approach in the development of new ESIPT fluors.

EXPERIMENTAL

General.

All melting points were determined in unsealed capillary tubes in a heated oil bath (Thomas-Hoover Unimelt, Arthur H. Thomas Co.) using 76 mm immersion thermometers and needed no correction. Most stirring in round-bottomed flasks was done with teflon-coated magnets of prolate spheroid shape. Evaporations were carried out with a rotary evaporator at a final pressure of 15-30 torr. Most solids were dried in a vacuum oven at 15-30 torr. Thin-layer chromatography was carried out with Whatman MK6F silica 1 x 3 inch plates visualized with short- and long-wave ultraviolet light. Elemental analyses were done by Oneida Research Services, Rensselaer, NY. Infrared spectra were determined in potassium bromide pellets (unless noted otherwise) with a Perkin-Elmer 1600 series FTIR using a diffuse reflectance cell. Ultraviolet spectra were determined in cyclohexane with a Shimadzu UV 265 (unless noted otherwise). The dilute solution method was used to determine Φ with a Farrand Spectrofluorometer Mk. I rebuilt to produce corrected spectra to 750 nm by Optical Technology Devices, Elmsford, NY (unless noted otherwise). The reference standard was the oxazole "Ox 2" of Φ = 0.73 in absolute ethanol [21]. The working equation was:

$$\Phi_{spl.} = (\Phi_{std.})(\text{Area}_{spl.})(\text{Absorbance}_{std.}) / (\text{Area}_{std.})(\text{Absorbance}_{spl.})$$

2'-Hydroxy-3',5'-dimethylacetophenone (**4b**).

The procedure for the Fries rearrangment of phenyl acetate [22] was applied to 2,4-dimethylphenol (Lancaster 7352) to give 43% of 4b, mp 53-55° (lit [23] mp 53-54°).

4-(3,3-Dimethyl-1-butoxy)benzaldehyde (**3c**).

A 250 ml 3-necked flask on a heating mantle with a stirring bar, thermometer, nitrogen inlet, reflux condenser topped with a Drierite tube, and a stopper was purged with nitrogen overnight at 52°. To the flask were added 4-hydroxybenzaldehyde (10.71 g, 0.0875 mole, Kodak 985), acetone (150 ml, Fisher Reagent), potassium carbonate (12.2 g, 0.0878 mole, Baker purified), and 1-bromo-3,3-dimethylbutane (20.7 g, 0.125 mole, [24]). The mixture was boiled under gentle reflux with stirring for 2 days and allowed to cool. The salts were filtered off and the filtrate evaporated. The residue was partitioned between 50 ml each of water and *t*-butyl methyl ether. The organic layer was washed with 60 ml of 2 *M* sodium hydroxide, then 20 ml of water, and then dried over 3 g of calcium chloride. Filtration through Whatman 1PS paper was followed by evaporation to 10.5 g of yellow oil which was then distilled using a spray trap. When the excess 1-bromo-3,3-dimethylbutane had distilled, the product was collected at 102-108°/0.05 torr to give 5.7 g of colorless oil (31%); ir (3.6% in carbon tetrachloride): 2710 (ArC*H*O), 1682 (C=O), 1242 (Ar-O-R). Its identity was confirmed by conversion to flavone **5c**.

7-*t*-Amyl-9,9-diethylfluorene-2-carboxaldehyde (**3f**).

Following Comins and Meyer's prodedure [10], a 250 ml 3-necked flask on a heating mantle with a stirring bar, thermometer, nitrogen inlet, reflux condenser topped with a Drierite tube, and a powder funnel replaced later with a 125 ml addition funnel was charged with magnesium (0.99 g, 0.041 mole, Reade RMC-3) and baked overnight at 50 V under nitrogen. A solution of 2-bromo-7-*t*-amyl-9,9-diethylfluorene (**1f**, 15.14 g, 0.041 mole, [19]) in 100 ml of anhydrous tetrahydrofuran (Aldrich 29,310-5) was placed in the addition funnel, and 10 ml of this solution was added to the reactor followed by 1 drop of 1,2-dibromoethane. The reaction started, so the rest of the solution was added dropwise during 3 hours, along with 1 drop of 1,2-dibromoethane after 1.5 hours and another after 3 hours; this was followed by an hour at reflux and then allowing the mixture to cool to 20° overnight. The cloudy mixture was heated to 50° and transferred under positive nitrogen pressure to an addition funnel mounted on a 500 ml 3-necked flask equipped as above, except for use of an ice bath; but containing a solution of *N*-methyl-*N*-(2-pyridyl)formamide (5.00 g, 0.0367 mole, Aldrich 23,654-3) in 50 ml of freshly distilled tetrahydrofuran cooled to 0°. The Grignard reagent was added dropwise at 0-5°, followed by 2.5 hours of stirring. As shown by tlc (developed with ethyl acetate), all *N*-methyl-*N*-(2-pyridyl)formamide was consumed. The mixture was poured into 100 ml of 5% hydrochloric acid pre-cooled on ice; the organic layer separated, and the aqueous layer was extracted with 3 x 40 ml of ether. The combined organic layers were washed with conc. sodium chloride solution, dried over sodium sulfate, and evaporated to yield 13.3 g of brown oil, which was distilled, bp 120-160°, mostly 150-160° at 0.1 torr, to give 9.12 g (78%) of yellow oil; ir (potassium bromide): 1695 (C=O).

Anal. Calcd. for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 86.48; H, 9.01.

7-(4-*t*-Butylphenyl)-9,9-dipropylfluorene-2-carboxaldehyde (**3g**).

Method A. By Reaction of Grignard Reagent with *N*-Methyl-*N*-(2-pyridyl)formamide.

Treatment of 2-bromo-7-(4-*t*-butylphenyl)-9,9-dipropylfluorene (**1g**) as above gave a brown oil which was recrystallized 3 times from hexane at -2° to give 12% of aldehyde, mp 149-150°; ir (potassium bromide): 1696 (C=O). An oxime was prepared, and a 2,4-dinitrophenylhydrazine test was positive; but satisfactory assays were not obtained.

Concentration of liquors gave 6% additional product, mp 145-150°.

Method B. By Reaction of Grignard Reagent with *N,N*-Dimethylformamide [11].

A 250 ml 3-necked flask on a heating mantle with a stirring bar, thermometer, argon inlet, reflux condenser topped with a Drierite tube, and a 125 ml addition funnel was charged with magnesium (0.973 g, 0.0400 mole, Reade RMC-3) and baked overnight at 75° under argon. A warm solution of 2-bromo-7-(4-*t*-butylphenyl)-9,9-dipropylfluorene (**1g**, 18.46 g, 0.0400 mole, [19]) and methylmagnesium chloride solution (1 ml, Aldrich 18,990-1) in anhydrous tetrahydropyran (100 ml, Aldrich 29,310-5) was added during 40 minutes near the boiling point, followed by 2 hours at reflux. The reactor was cooled in ice to 0°. A solution of *N,N*-dimethylformamide (2.95 ml, 2.78 g, 0.0381 mole, HPLC Grade, Aldrich 27,054-7) in 30 ml of anhydrous ether was added below 7° during 10 minutes. The mixture was warmed to 25° for 1 hour, then 40 ml of 3 *M* hydrochloric acid was added rapidly, which caused an exotherm to 32°, and the *p*H to drop to ≈ 1. The organic layer was washed with a solution of 5.4 g of sodium bicarbonate in 60 ml of water, dried over 5 g of magnesium sulfate, and evaporated to 16.47 g of gum, which was crystallized from 50 ml of heptane at 22° to give 12.1 g (78%) of pale yellow solid, mp 142-144°.

The analytical sample was obtained by recrystallizing 0.3 g from 10 ml of heptane at 20°, pale yellow prisms, mp 142-144°.

Anal. Calcd. for $C_{30}H_{34}O$: C, 87.74; H, 8.36. Found: C, 87.89; H, 8.50.

6,8-Dimethyl-2-phenyl-3-hydroxy-4-chromenone (**5b**).

A solution of 6.0 g of potassium hydroxide (87% potassium hydroxide pellets, U. S. P.) in 10 ml of water was prepared, cooled to ≈ 20°, and poured into a magnetically stirred solution of 2'-hydroxy-3',5'-dimethylacetophenone (4.5 g, 0.0277 mole, **4** where $R=CH_3$) and benzaldehyde (2.9 g, 0.0277 mole, Amend) in 37 ml of 95% ethanol in a 1 ℓ flask in an empty ice bath. A deep orange color developed. After 3 hours of stirring, the mixture was kept at ≈ 20° overnight. Then 200 ml of 95% ethanol was added, followed by a cool solution of 3 g of potassium hydroxide in 9 ml of water, and 30 ml of 30% hydrogen peroxide. A yellow precipitate formed and turned brown. After 20 minutes, ice was added to the bath, and 100 ml of water to the reactor. The now yellow suspension was brought to *p*H ≈ 6 with 6.5 ml of 12 *N* sulfuric acid and stirred 1 hour, filtered, and dried at 60°/6 hours to give 9.0 g of crude product, which was extracted with 160 ml of toluene from a medium Soxhlet for 8 hours. The extract was concentrated to 75 ml and kept at -5° to give 0.59 g (8%) of product after drying; mp 221-223°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.67; H, 5.34.

2-[4-(3,3-Dimethylbutyl)phenyl]-3-hydroxy-4-chromenone (**5c**).

The procedure described above for **5b** was applied to 4-(3,3-dimethyl-1-butoxy)benzaldehyde (5.70 g, 0.0277 mole, **3c**) and 2'-hydroxyacetophenone (3.77 g, 0.0277 mole, Aldrich H1,860-7, **4** where R = H) to give 15.3 g of crude product. This was extracted from a medium Soxhlet with 200 ml of cyclohexane to obtain all fluorescent material, 4.5 hours, and the extract of 150 ml was diluted with 100 ml of hexane and kept at 0° overnight to give 5.03 g (54%) of pale buff solid, mp 124-125°; pmr, Bruker NR-80 (2% in deuteriochloroform): δ 1.03 (s, 9H, $CH_2(CH_3)_3$), 1.43 (s, ≈ 0.4 H, H_2O), 1.58 (br s, 1H, 3-O*H*), 1.78 (t, 2H, J = 7.2 Hz, $CH_2(CH_3)_3$), 4.13 (t, 2H, J = 7.2 Hz, OCH_2), 6.8-8.4 ppm (m, 8H, Ar*H*).

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.83; H, 6.53.

3-Hydroxy-2-naphthyl-4-chromenone (**5d**).

The procedure described above for **5b** was applied to 2-naphthaldehyde (5.00 g, 0.0320 mole, Aldrich N20-6) and 2'-hydroxyacetophenone (4.35 g, 0.0320 mole, Aldrich H1,860-7, **4** where R = H) to give 7.07 g of crude product. This was extracted from a small Soxhlet with 150 ml of cyclohexane to obtain all fluorescent material, 6 days, and the extract was kept at 20° overnight to give 3.89 g (42%) of pale yellow solid, mp 202-204°.

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.16; H, 4.20. Found: C, 79.05; H, 4.25.

2-(4-Biphenylyl)-3-hydroxy-4-chromenone (**5e**).

The procedure described above for **5b** was applied to 4-biphenylcarboxaldehyde (5.00 g, 0.0275 mole, Aldrich B3,468-0) and 2'-hydroxyacetophenone (3.73 g, 0.0275 mole, Baker N476, old, **4** where R = H) to give 6.00 g of crude product. This was recrystallized from 225 ml of *p*-xylene to give 4.12 g (48%) of lemon yellow needles, mp 223-226° (lit 220-222° [7], 222-223° [25]).

2-(7-*t*-Amyl-9,9-diethyl-2-fluorenyl)-3-hydroxy-4-chromenone (**5f**).

Method A. Tetrahydrofuran and 95% Ethanol as Initial Solvents.

The procedure described above for **5b** was applied to a solution of 7-*t*-amyl-9,9-diethylfluorene-2-carboxaldehyde (**3f**) in 1:4:8 water:ethanol:tetrahydrofuran. No pure chromenone was isolated from the orange solid obtained.

Method B. Dioxane and Absolute Ethanol as Initial Solvents.

The procedure described *below* for **5g** was carried out with 7-*t*-amyl-9,9-diethylfluorene-2-carboxaldehyde (2.56 g, 0.00800 mole, **3f**). The gummy crude product was dried at 22°/0.4 torr/72 hours, then extracted from a medium Soxhlet thimble with 60 ml of heptane for 8 hours. The extract was cooled at -20° to give 0.65 g of a yellow solid after filtration and drying as before, mp 110-120°. This solid was chromatographed on 20 g of Silica Gel (Aldrich 24,217-9 equivalent to Merck 10181) in a

2 cm diameter column, eluting with 5% ethanol in cyclohexane. Evaporation gave 0.5 g of solid which was recrystallized from 10 ml of heptane at 22° to give 0.38 g, mp 135-140°; again from 8 ml of heptane to give 0.32 g, mp 138-143°; again from 15 ml of methanol, cooling to -20°, to give 0.22 g (6%), mp 172-173.5°; the major spot on tlc had $R_f = 0.5$ (10% ethanol in cyclohexane); very minor spots had lower R_f and similar yellow fluorescences; pmr, see Table 3.

Anal. Calcd. for $C_{31}H_{32}O_3$: C, 82.27; H, 7.13. Found: C, 81.89; H, 6.97.

2-[7-(4-*t*-Butylphenyl)-9,9-dipropyl-2-fluorenyl]-3-hydroxy-4-chromenone (**5g**).

Method A: Tetrahydrofuran and 95% Ethanol as Initial Solvents.

The procedure described above for **5b** was applied to a solution in 20 ml of tetrahydrofuran and 10 ml of 95% ethanol of 7-(4-*t*-butylphenyl)-9,9-dipropylfluorene-2-carboxaldehyde (1.27 g, 0.0031 mole, **3g**) and 2'-hydroxyacetophenone (0.42 g, 0.0031 mole, Aldrich H1,860-7, **4** where R = H) to give 1.27 g of crude product. This was extracted from a small Soxhlet with 50 ml of toluene to obtain all fluorescent material, 12 hours; the extract was evaporated, and the residue recrystallized from 60 ml of ethanol at -20° to give 0.193 g (11%), mp 225-227°.

Anal. Calcd. for $C_{38}H_{38}O_3$: C, 84.10; H, 7.06. Found: C, 84.10; H, 7.11.

Method B. Dioxane and Absolute Ethanol as Initial Solvents.

A solution of 5.6 g of potassium hydroxide (87%, U. S. P.) in 100 ml of ethanol was prepared, cooled to ≈ 20°, and poured into a solution of 2'-hydroxyacetophenone (4.0 g, 0.0031 mole, Aldrich H1,860-7, **4** where R = H) and 7-(4-*t*-butylphenyl)-9,9-dipropylfluorene-2-carboxaldehyde (11.8 g, 0.0288 mole, **3g**) in 200 ml of *p*-dioxane in a 2 ℓ flask in an empty ice bath while stirring magnetically. A dark yellow color developed. After 15 minutes of stirring, the mixture was kept at ≈ 20° overnight, when the blue phosphorescence of the aldehyde was no longer visible. A cool solution of 3 g of potassium hydroxide in 9 ml of water was added, and 30 ml of cold 30% hydrogen peroxide. An exotherm to 32° was observed, and 2 liquid phases appeared. After 2 hours, ice was added to the bath, and 400 ml of water to the reactor. The now yellow suspension was brought to *p*H 4.5 as determined by narrow-range pHydrion paper, with ≈ 55 ml of 1:25 sulfuric acid:water and stirred 1 hour, filtered, and dried at 100°/20 torr/1 hour to give 17.66 g of crude product, which was recrystallized from 180 ml of dibutyl ether, after filtering while hot through Whatman 1PS paper. The yellow spars were filtered with suction, washed with 25 ml of methanol, and dried at 125°/15 torr/2 hours to give 3.57 g (23%) of product, mp 238-239.5°; pmr, see Table 2.

Anal. Calcd. for $C_{38}H_{38}O_3$: C, 84.10; H, 7.06. Found: C, 83.83; H, 7.08.

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