Syntheses and Photophysical Properties of Some 4-Arylpyridinium Salts

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A number of 4-arylpyridines, many methoxy substituted, were prepared by an efficient two-step method involving aryl Grignard addition to 1-methyl-4-piperidone and direct aromatization of the resulting 4-aryl-4-piperidinols. The pyridines were *N*-alkylated to give sulfonate salts desired for their fluorescent properties. Study of selected compounds as laser dyes revealed several structures to be efficient dyes lasing in the 530-550 nm range. Two new diazaquaterphenyls were prepared and were quaternized. These salts exhibited intense fluorescence in the 420-450 nm range, but would not lase. A phenolic azaterphenyl suitably substituted for excited state intramolecular proton transfer (ESIPT) did not fluoresce at all.

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Introduction.

The report [1] of the exceptional service lifetime as a laser dye of 5-(4-methoxyphenyl)-2-(4-pyridyl)oxazole **1**, as its methyl *p*-toluenesulfonate quaternary salt **2C**, has inspired the synthesis of a number of heterocyclic analogs of **1** in which both the pyridine and oxazole rings were preserved [2]. In this paper, we report the synthesis of a number of analogs of **1** which are 4-arylpyridines (4-azaterphenyls) in which the central oxazole has been replaced by a benzene ring. That the oxazole ring might be a point of instability was suggested by early work in which the presence of 2,5-disubstituted oxazole rings in known fluorescent scintillators had been shown to lead to photodecomposition of the chromophore on prolonged irradiation in air [3]. Since we have previously reported on the marked photochemical stability of oligophenylenes under conditions of high intensity irradiation [4,5], we sought to prepare a series of fluorescent pyridinium salts which contained both unbridged and bridged carbocyclic aromatic rings on C-4 of the pyridine ring. Most of these salts contain a methoxy substituent placed so as to allow its conjugation to the quaternized pyridinium ring. In a few compounds electron release was provided without a methoxy group by a dialkylmethylene bridged biphenyl (a fluorene) or by a carbazole ring.

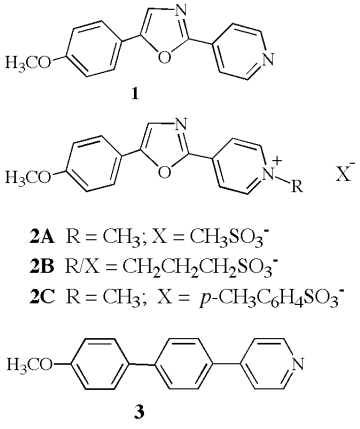


Figure 1. 4-Arylpyridines and Quaternary Salts.

Most of these new 4-arylpyridines were quaternized by alkylation with sulfonate esters, whose structures were optimized in an earlier study on derivatives of **2** [6,7] and were tested for fluorescence efficiency and as laser dyes in alcohol-water mixtures. Compounds of this type have also shown enhanced lasing properties in aqueous sodium dodecyl sulfate solutions [8].

In initiating this study, we sought in three ways to improve upon the lasing properties of **2C** and its oxazole-containing analogs to obtain laser beams better able to penetrate sea water: (a) achieve a higher level of power output; (b) induce a hypsochromic shift in the wavelength of fluorescence (lasing) to more closely approach 490 nm, the wavelength of maximum transmission of sea water, and (c) to get (even) more service lifetime out of the dyes in order to decrease the need for recurring solvent changes in the dye laser.

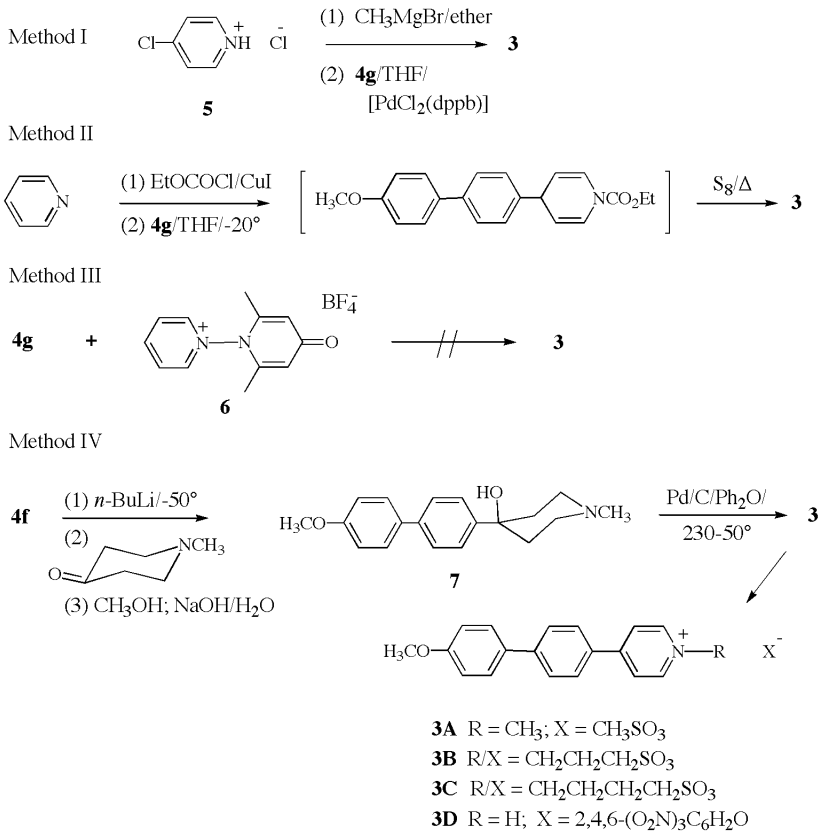
In an attempt to discover whether the 4-arylpyridine chromophore could experience excited state intramolecular proton-transfer (ESIPT) fluorescence, we designed a molecule in which a phenolic hydroxyl group could deliver a proton to the pyridine nitrogen.

Discussion and Results.

Syntheses.

Our first target was the simplest analog azaterphenyl **3** in which the oxazole ring in **1** was replaced with a phenylene unit. For any synthesis of 4"-methoxyazaterphenyl **3**, we required 4-bromo-4'-methoxybiphenyl, **4f** as the starting material. Reaction of 4-methoxybiphenyl **4a** in chloroform with 1.0 equivalent of bromine gave **4f** in the reported [9] 20% yield and melting range after two crystallizations from chloroform. The byproducts, identified by HPLC as major amounts of unreacted **4a**, a monobromo derivative

Scheme 1
Preparation of 4"-Methoxy-4-azaterphenyl (**3**)



3A R = CH_3; X = CH_3SO_3
3B R/X = $CH_2CH_2CH_2SO_3$
3C R/X = $CH_2CH_2CH_2CH_2SO_3$
3D R = H; X = 2,4,6-$(O_2N)_3C_6H_2O$

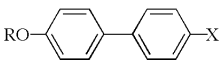
isomeric with **4f** and a dibromo derivative of **4a**, indicated similar bromination rates in both the phenyl and the methoxyphenyl rings of **4a**.

Carbonate esters of **4b** were known to brominate in the 4'-position in halocarbon solvents [10,11]. We observed the bromination of 4-benzoyloxybiphenyl **4c** at 80° in acetic acid exclusively in the 4'-position to give **4d** in exceptional yield. Experiments with 4-acetoxybiphenyl gave lower yields and partial hydrolysis on oven drying. Hydrolysis of **4d** gave phenol **4e** [10] which upon *O*-methylation gave **4f**.

To prepare the azaterphenyl **3**, bromobiphenyl **4f** was converted to the corresponding Grignard reagent **4g** in concentrated tetrahydrofuran solutions. Formation of Grignard **4g** was not efficient in dilute solutions. In Method I, **4g** was reacted in the presence of a palladium (II) catalyst with 4-chloropyridine (liberated *in situ* from its hydrochloride salt **5** by the prior addition of methyl Grignard) to give **3** directly in moderate yield. In Method II following Comins and Abdullah [12], Grignard **4g** was reacted with pyrdine, which had been activated *in situ* with ethyl chloroformate, to yield a crude *N*-acyl-1,4-dihydropyridine which was aromatized directly by heating with sulfur [12] in refluxing mesitylene [13]. The sample of **3** which resulted from this two-step pathway possessed a depressed melting range even after sublimation, most likely because of the presence of a regioisomer [12], was purified as its picrate salt **3D** and re-isolated as the free base **3** in just 9% yield.

In an attempt to eliminate regioisomer formation, we reacted Grignard **4g** with the highly sterically hindered quaternary pyridinium salt **6** [14], Method III in Scheme 1. No trace of **3** was isolated from this reaction.

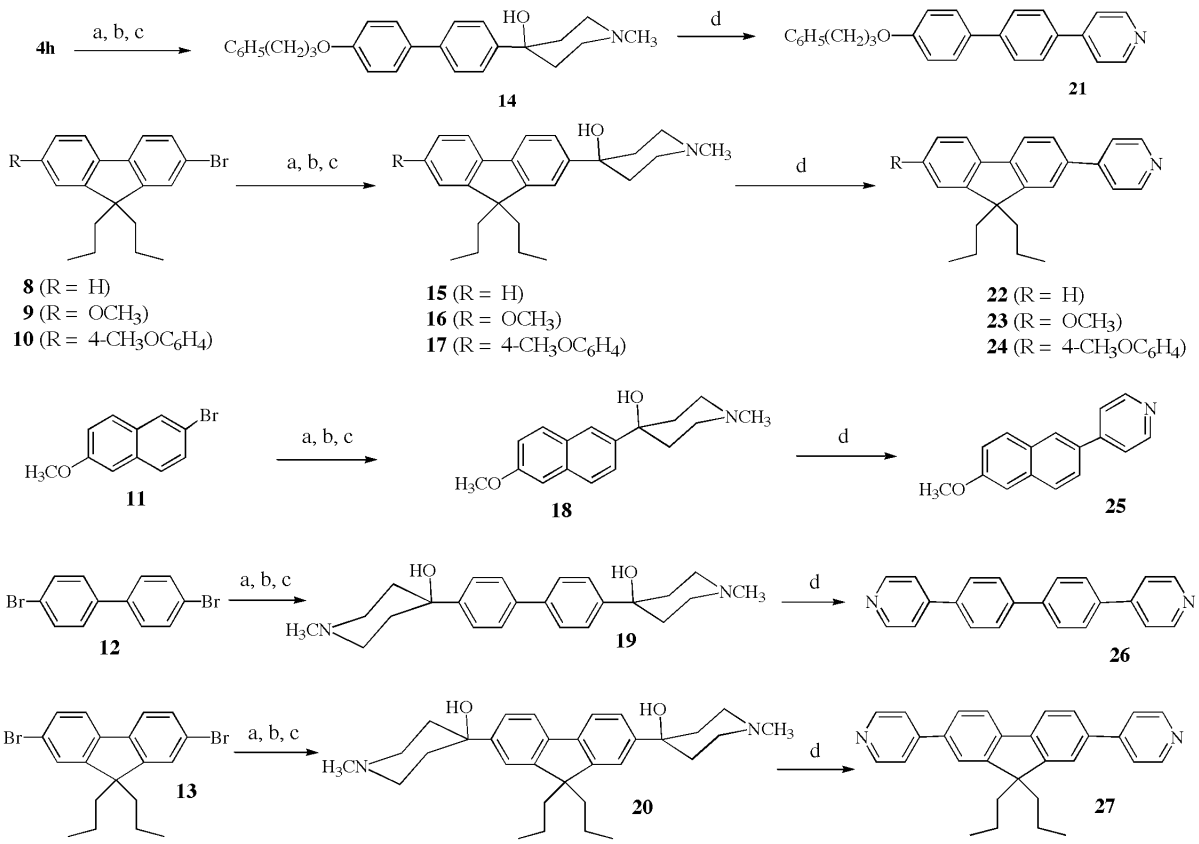
Subsequently, we developed Method IV employing classical pharmaceutical piperidinol [15,16] intermediates in an efficient two-step synthesis of **3**. The lithium



4a R = CH_3; X = H
4b R = X = H
4c R = PhCO; X = H
4d R = PhCO; X = Br
4e R = H; X = Br
4f R = CH_3; X = Br
4g R = CH_3; X = MgBr
4h R = $PhCH_2CH_2CH_2$; X = Br

Figure 2. Biphenyls Used to Synthesize Azaterphenyls.

Scheme 2
Preparation of Other 4-Arylpyridines Through N-Methyl-4-piperidinol Intermediates.



Reagents: (a) *n*-BuLi/THF/-50°; (b) *N*-methyl-4-piperidone; (c) methanol, then aqueous sodium hydroxide; (d) Palladium on carbon/diphenylmethane (or diphenyl ether)/240°.

derivative from transmetalation of bromobiphenyl **4f** was reacted at low temperature [16] with 1-methyl-4-piperidone to give the 4-aryl-4-piperidinol **7**.

Aromatization of the saturated heterocyclic ring of **7**, which involves first the loss of water from the tertiary benzylic alcohol and then loss of hydrogen and methane, was first carried out in refluxing nitrobenzene. However, azaterphenyl **3** could not be extracted into aqueous hydrochloric acid. Aromatization of dihydroarenes over palladium on carbon are well known [17]. We found that piperidinol **7** was only partially aromatized during 72 hours in refluxing mesitylene. Aromatization was completed by heating **7** overnight at higher temperatures in refluxing diphenylmethane or diphenyl ether under a nitrogen purge [17] to remove the water and gaseous byproducts.

This two-step method was employed as shown in Scheme 2 to convert aryl bromides **4h**, 2-bromofluorenes **8-10**, bromonaphthalene **11**, and diaryl dibromides **12** and **13** to piperidinols **14-18** and bispiperidinols **19** and **20**. Aromatization of the piperidinols over palladium on carbon in diphenyl ether or diphenylmethane at elevated temperatures gave pyridines **21** to **25** and bispyridines (diazaquaterphenyls) **26** and **27**. Azaterphenyls **22** and **23**, azaquaterphenyl **24** and diazaquaterphenyl **27** contained bridging dipropylmethylene groups for greater coplanarity of the multiaryl systems.

Correspondingly prepared by the sequences shown in Scheme 3 were 6-methoxy-2-naphthyl derivative **29** and carbazole derivative **33**. Compounds **29** and **33** were synthesized from 4-(4-chlorophenyl)pyridine **28**. The Grignard reagent from aryl bromide **11** produced **29** by nickel-catalyzed coupling, while the Grignard reagents from **31** gave **33** with palladium coupling. Although **28** is a known compound, literature methods reported for its synthesis gave mixtures of regioisomers [18,19]. Thus we prepared **28** from **5** by the Method I of Scheme 1.

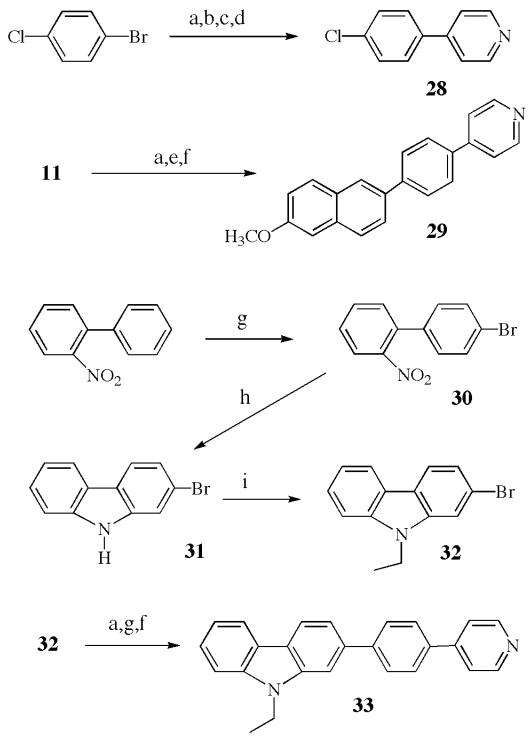
Each of the new pyridines (except **33**) was quaternized with methyl methanesulfonate and/or sultones in nitrile solvents to give highly fluorescent salts soluble in polar

Table 1
Absorption and Lasing Propertiesof 4-Arylpyridinium Salts in Methanol

Compound Number	Longwave Ultraviolet Absorption max. (nm)	Lasing Output [a] (mJ)	Peak Lasing (nm)
2A	411 [b]	10.30 [c]	569 [c]
2B	410 [b]	13.06 [c]	572 [c]
3A	354	6.47	532
3B	357 [d]	15.3	548
22B	361	0.8	≈455
23B	380	9.4	530
25A	370	2	481
25B	367	no lasing	481 [e]

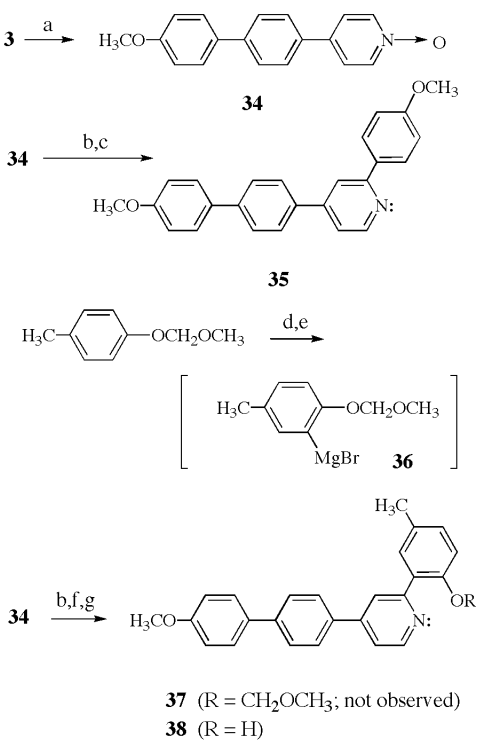
[a] In methanolic solution at 2 x 10^{-4}. [b] In ethanol from ref. [7]. [c] From ref. [6]. [d] 2.1 x 10^{-5} *M* in ethanol. [e] Peak fluorescence emission.

Scheme 3
Preparation of 4-(4-Chlorophenyl)pyridine **28**, 2-Bromo-9-ethylcarbazole **31** and Related 4-Arylpyridine **33**.



(a) Mg/Δ/THF; (b) **5**/[$PdCl_2$(dppb)]/Δ; (c) HCl/H_2O; (d) $NaHCO_3$; (e) **28**/Ni(AcAc)$_2$; (f) methanol; (g) Br_2/$FeCl_3$/CH_2Cl_2; (h) P(OCH$_2$CH$_3$)$_3$/Δ; (i) *t*-BuOK/CH_3SOCH_3/CH_3CH_2Br (g) **28**/$PdCl_2$ (dppb).

Scheme 4
Formation of Azaterphenyl N-oxide **34** and *ortho*-Arylation in the Pyridine Ring.



(a) *m*-chloroperoxybenzoic acid/$NaHCO_3$/$CHCl_3$ (b) $ClCO_2CH_2CH_3$/25°; (c) 4-$CH_3OC_6H_4MgBr$; (d)*n*-BuLi/THF/-60° to 25°; (e) $MgBr_2$/THF/20°; (f) cool to -50°; (g) **36**

organic solvents. Quaternizations with 1,3-propane sultone were conveniently completed within minutes in hot benzonitrile in which the high melting salts had some solubility. The lower melting quaternary salts from methyl methanesulfonate were in some cases more conveniently isolated after their formation during extended periods of reflux in acetonitrile.

To prepare a modification of azaterphenyl **3** that would provide a suitable test of the effects of intramolecular proton transfer, we converted **3** to its *N*-oxide **34** and used the method of Webb [20] to activate the pyridine ring for introduction of the *p*-anisyl group in the 2-position to give **35**. Then we metalated methoxymethyl *p*-tolyl ether with *n*-butyllithium, converted to the Grignard with magnesium bromide, and reacted the Grignard with the activated *N*-oxide to give the phenolic **38** directly, as the methoxymethyl group from **37** was lost in the workup. The product **38**, obtained in only 2% yield, was fully characterized by hi-field nmr.

Photophysical Properties.

The ultraviolet absorption spectra of bridged and unbridged azaterphenyls resemble closely the published data for similarly substituted terphenyls [21]. The

quaternization of the pyridine ring in 4"-alkoxyazaterphenyls causes a substantial bathochromic shift in their ultraviolet absorption spectrum, presumably through the enhanced contribution of resonance forms in which oxygen releases non-bonding electrons to the pi system with the positively charged nitrogen at its other terminus.

A comparison of the ultraviolet absorption data in Table 1 for azaterphenyl quaternary salt **3A** with a phenylene middle ring to **2A** with its oxazole ring reveals a 51 nm hypsochromic shift for the replacement of the internal oxazole by a phenylene. A similar hypsochromic shift is observed in comparing ring bridged analog **23B** with unbridged **3B**. These shifts reflect both the electronic nature of the oxazole [2] and the greater energy required for the phenylene ring of **3A** with four buttressing hydrogen atoms in a six-membered ring to be converted from a non planar ground state into a necessarily planar excited state. In **23B** only the pyridine ring needs to come into planarity with the fluorene in the excited state. Fluorescent carbocyclic chromophores exhibit similar relationships between bridged and unbridged compounds [21].

The quaternary salts of the 4-arylpyridines prepared in this study were all fluorescent. Representative strongly fluorescent compounds were subjected to lasing experiments as shown in Table 1. As was anticipated, the peak lasing occurred at shorter wavelengths for **3A/B** and **23B** than had been observed for the oxazoles **2A/B**. This paralleled closely the hypsochromic shift in peak lasing reported for *p*-terphenyl versus 2,5-diphenyloxazole [3]. The energy output for **3B** (15.3 mJ) was the highest output yet observed in alcohol solvents among all compounds of the quaternary 4-arylpyridinium class. Service lifetime experiments were not conducted, but no deterioration in output power was observed during the periods studied.

In a related experiment, **3B** was observed to lase with moderate efficiency at 545 nm in solid polymethyl methacylate plastic rod when pumped with 355 nm light from a YAG laser [22].

Relative lasing efficiencies within the oxazole series [6,7] were maintained in the phenylene series *N*-methyl to *N*-methyl, and zwitterion to zwitterion, and there was no loss of lasing efficiency. In these respects our original goal was achieved. Ring bridging with dipropylmethylene groups, however, showed none of the enhancements in lasing which were observed with oligophenylenes [23] either in wavelength or in efficiency, which actually decreased for the compounds with bridging. The only beneficial effect of ring bridging was qualitatively demonstrated by the fluorescence of azaquaterphenyl salt **24a** in which bridging of the central fluorene unit allowed the transmission of electron donation by the methoxy group to extend through 4 aromatic rings.

Weak lasing was observed for compounds **22B** in which a fluorene ring alone provided electron release to the quaternary pyridinium, and also for **25A** in which the 6-methoxy-2-naphthyl group was the electron releaser. In the latter system, the methoxy is one double bond closer to the pyridinium ring than in compound **3A**. Much of the 50 nm hypsochromic shift in lasing could be attributed to the missing double bond. The weak lasing observed for **25A** frustrated our aim of obtaining useful compounds lasing around 490 nm.

In an additional attempt to prepare compounds with shorter wavelength fluorescence, we prepared two diazaquaterphenyls **26** and **27** and their quaternary salts. The ultraviolet spectra for these quaternary salts were bathochromically shifted 45-50 nm from absorptions of corresponding quaterphenyls, and exhibited comparable extinction corefficients [21]. The fluorescence quantum efficiency of **26A** in methanol was about 1.0, while **27A** was 0.82, but neither would not lase flashlamp pumped [24]. The durabiltiy of the fluorescence of these salts was verified by our observation that a methanolic solution of **26A** exposed to diffuse daylight was still exhibiting blue fluorescence after 11 years. A similar solution of the bridged analog **27A** showed a substantial loss of fluorescence during six years.

Although pyridine **35** was quite fluorescent, its phenolic isomer **38** not only did not exhibit ESIPT fluorescence, but it did not fluoresce at all. In known ESIPT fluors [25], the proton transferred from the phenol in the excited state is accepted by a heterocyclic nitrogen much less basic than a pyridine ring. The failure of **38** to fluoresce may be related to the proximity of pKa values between the phenol and the pyridine nitrogen to which, as evidenced by its strongly deshielded chemical shift (14.2 ppm) in the nmr, it is strongly hydrogen bonded in the ground state. Indeed, it appears that the effect of the intramolecular proton transfer in **38** is to completely quench fluorescence.

EXPERIMENTAL

General.

The methods employed in references [2], [4] and [5] were followed with the following exceptions: 1-methyl-4-piperidone was purchased from Aldrich or Lancaster and stored in a refrigerator. On standing for more than one month, some samples showed increased viscosity and coloration. Vacuum distillation of older samples gave material of comparable quality to newly purchased material. Palladium(II) couplings were catalyzed by palladium(II) chloride 1,4-bis(diphenylphosphino)butane [(PdCl2(dppb)] prepared from palladium(II) chloride in 6 mL/mmol of dimethylformamide containing one millimolar equivalent of 1,4-bis(diphenylphosphino)butane by heating at reflux for several hours as the color progressed from gray through yellow to green, cooling, filtering, and washing with ether. Anhydrous sodium sulfate, magnesium sulfate and calcium chloride were used to dry solutions. 6-Bromo-2-naphthol (Aldrich B7,340-6) was methylated by the procedure for **4f** to give **11**; methyl methanesulfonate (Aldrich 12,992-5),1,3-propane sultone (Aldrich P5,070-6), 1,4-butane sultone (Aldrich B8,550-1) nickel acetylacetonate (Aldrich 28,365-7),

n-butyllithium as a solution in *n*-hexane (2.1 *M*, 2.5 *M*, Aldrich, or 2.2 *M*, Alfa) were used as received. Pentene (technical, T418) purchased from Eastman Kodak is no longer commercially available in useful quantities. Most ^{1}H nmr spectra were recorded at 60 MHz in deuteriochloroform with internal tetramethylsilane except where stated that the solvent was trifluoroacetic acid (non-deuterated) referenced to external tetramethylsilane in choroform. Laser experiments were performed under conditions stated [6].

4-Benzoyloxybiphenyl (**4c**).

A slurry of 4-phenylphenol (**4b**, 252 g, 1.48 mol) in benzoyl chloride (172 mL, 208 g, 1.48 mol) was mechanically stirred as 300 mL of pyridine was added in small portions. The resulting warm solution was heated to reflux for 30 minutes, was cooled, filtered, washed with 2 L of 1% hydrochloric acid, and a larger portion of water. The solid was air-dried to give 404 g (99%) of **4c**, mp 150-152°; Lit. [26] mp 149-150.5°.

4-Benzoyloxy-4'-bromobiphenyl (**4d**).

A mixture of 400 g (1.46 mol) of **4c** and 150 g, (1.82 mol) sodium acetate in 0.9 L of acetic acid became homogeneous on being heated to 90° with mechanical stirring. Bromine (87 mL, 269 g, 1.68 mol) was added to the solution in portions during 4 hours, and stirring and heating at 90° were maintained for 20 hours. The solution was diluted with 0.6 L of 10% aqueous sodium bisulfite and 1.0 L of water. The precipitate collected by filtration was air-dried, to give 506 g (98%) of **4d**, mp 179-181°. A 250 g portion of crude **4d** was dissolved completely in 3 L of acetic acid upon boiling for 40 minutes. Crystallization overnight at room temperature gave 242 g (97% recovery.) of **4d**, mp 188-190°; Lit. [10] mp 187.5-188.5°.

4-(4-Bromophenyl)phenol (**4e**).

A mechanically stirred mixture of 336 g (0.94 mol) of **4d**, 161 g of potassium hydroxide, 940 mL of dimethyl sulfoxide, and 2 L of water was refluxed. After 1 hour all solids had dissolved; after 4 hours the solution was cooled to 65°, and 200 mL of acetic acid was added in portions. The granular solid which separated after the mixture had cooled to room temperature was filtered, washed with 500 mL of 10% sodium bicarbonate, with several liters of water, and air-dried to give 246 g (104%) of **4e**, mp 143-145°; Lit. [10] mp 144-145.5°.

4-Bromo-4'-methoxybiphenyl (**4f**).

To a slurry of 148 g (0.6 mol) of **4e**, 25 g of sodium hydroxide in 700 mL of water and 1.8 L of dimethyl sulfoxide, was added dropwise 56.8 mL (75.7 g, 0.6 mol) of dimethyl sulfate. The mixture was refluxed for 3.5 hours, and all solids dissolved. The mixture was diluted with water and filtered to give 141.2 g (89%) of **4f**, mp 144.5-146°; Lit. [9] mp 143-4°.

4-(4'-Methoxybiphenyl-4-yl)pyridine [4''-methoxy-4-azaterphenyl] (**3**).

Method I.

A flask containing magnesium turnings (0.915g, 38 mmol), was flame-dried under nitrogen purge, was cooled, and 10.0 g (0.0380 mol) of **4f** and 6 mL of tetrahydrofuran were added. The mixture was heated to reflux, causing the color to darken within 5 minutes. During the next 3 hours, 60 mL of tetrahydrofuran was added in small portions to the refluxing mixture as the magnesium dissolved to produce the solution of **4g**.

In a separate flask was placed 2.87 g, (19.2 mmol) of 4-chloropyridine hydrochloride **5** and 20 mL of tetrahydrofuran. The mixture was stirred while 6.8 mL (19 mmol) of 2.85 *M* methylmagnesium bromide diluted with 20 mL of THF was added slowly. The evolution of methane ceased when about 80% of the solid had dissolved. To this mixture was added in one portion the Grignard **4g**. No change was observed during 10 minutes stirring at room temperature. Palladium(II) chloride 1,4-bis(diphenylphosphino)butane (0.174 g, 0.29 mmol) was added to the mixture. All solids dissolved in 10 minutes, stirring was continued for 12 hours, an additional 0.058 g of palladium catalyst was added, and the solution was stirred for 24 hours. Methanol (20 mL) was added dropwise, and all solvents were evaporated. The semi-solid was dissolved in methylene chloride and was pre-adsorbed on Silica Gel (20 g) under reduced pressure. The dry mixture was placed atop 150 g of Silica Gel in a large Ace-Kau column, and extracted with boiling pentene to remove 2.54 g of 4-methoxybiphenyl (**4a**). Further extraction for 24 hours with methylene chloride gave traces of a fluorescent, high-melting solid believed to be 4,4'''-dimethoxyquaterphenyl. Continued extraction for another 24 hours with the azeotropic mixture of ethyl acetate/methanol (51.4:48.6%) gave a semi-solid after evaporation of solvents. Digestion with 30 mL of 95% ethanol gave after filtration, 1.58 g of **3**, mp 225-238°. Recrystallization from 30 mL of 2-methoxyethanol gave 1.20 g (24%) of **3**, mp 229-230°.

Anal. Calc. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.60; H, 6.08; N, 5.25

Method II.

A flask containing ground magnesium pieces (2.4 g, 0.1 mol) was flame-dried under a stream of nitrogen and allowed to cool. Tetrahydrofuran (30 mL) and **4f** (26.3 g, 0.l mol) were added and after ten minutes heating with stirring, the solid dissolved and the mixture darkened as the exothermic reaction carried the temperature to 74°. After the exotherm subsided, the mixture was diluted with 30 mL of tetrahydrofuran and was refluxed for 3 hours to give the solution of **4g**.

Into a separate flask equipped with a mechanical stirrer, under nitrogen was added l.27 g of copper(I) iodide, 16.1 mL of pyridine (0.20 mol, dried over KOH) and 200 mL of tetrahydrofuran. To the stirred, cooled (-20°), yellow solution was added 12.8 mL (0.134 mol) of ethyl chloroformate dropwise during 15 minutes. The yellow precipitate which formed was vigorously stirred while the solution of **4g** was added dropwise during one hour at -20°. During an additional hour of vigorous stirring, the temperature was allowed to slowly rise to room temperature. Aqueous ammonium chloride (20%, 75 mL) and ethyl acetate (200 mL) were added and two layers separated. The lower aqueous layer was discarded, and the organic layer was washed with 3x50 mL of a mixture of 20% ammonium chloride and ammonium hydroxide (1:1), 2x150 mL of water, 2x50 ml of 10% hydrochloric acid, 2x150 mL of water and saturated aqueous sodium chloride. The solution was dried over calcium chloride, and the solvent was removed under reduced pressure to give 27.0 g of a highly viscous yellow oil. Crystallization from a mixture of 30 mL of absolute ethanol and 50 mL of methanol gave 15.5 g of a yellow powder, mp 80-142°. Recrystallization from boiling ethanol (40 mL)

diluted with 40 mL of methanol at room temperature gave 9.7 g of the crude dihydropyridine [1-ethoxycarbonyl-4-(4'-methoxybiphenylyl)-1,4-dihydropyridine] melting began at 140° and was completed at 181-2° (dec.).

A mixture of the dihydropyridine (1.0 g, 3.13 mmol) and precipitated sulfur (0.12 g, 3.75 mmol, 20% excess) in 15 mL of mesitylene was heated for 4 hours in an oil bath at 154°. Filtration of the cooled mixture gave 400 mg of dark brown solid which was sublimed at 0.01 torr to give 183 mg of yellow material, mp 200-223°. The crude product was dissolved in 30 mL of boiling acetone, and a solution of 0.24 g of picric acid in 5 mL of acetone was added to the warm solution. The yellow precipitate was filtered and dried to give 207 mg of **3D**, mp 222° (dec). Recrystallization from acetone gave 143 mg of picrate **3D**, mp 224° (dec).

Anal. Calc. for $C_{26}H_{23}NO.0.85\ H2O$: C, 57.00; H, 3.93; N, 11.08. Found: C, 57.03; H, 3.68; N, 10.91.

Liberation of the free base with 5% NaOH solution allowed the isolation of 70 mg (8.5%) of **3**, mp 229-32°.

Method IV.

To 350 mL of diphenyl ether warmed to 140° was added 51.5 g of **7** and 2.5 g of 10% palladium on carbon. Nitrogen gas was bubbled through the mixture while it was heated at 230-255° during 24 hours. On cooling to room temperature, the mixture was filtered through a bed of Celite, and was washed with hexane. The mixture was placed atop more Celite in a large Ace Kau and was extracted with boiling methylene chloride (0.75 L) for 16 hours. Chilling and filtration gave 12.5 g of **3**, mp 225-7°. Successive concentration, chilling and filtration gave three additional crops bringing the yield of **3** to 31.3 g (69%).

4-Hydroxy-4-(4'-methoxybiphenyl-4-yl)-1-methylpiperidine (**7**).

A slurry of 26.3 g, (0.1 mol) of **4f** in 200 mL of tetrahydrofuran dissolved on heating under nitrogen. As the solution was cooled to -40°, a fine white precipitate separated, and 47.5 mL (0.1 mol) of *n*-butyllithium in hexane was added dropwise during 15 minutes below -40°. As a solution of 1-methyl-4-piperidone (13.5 mL, 10% excess) in 20 mL of tetrahydrofuran was added dropwise during 10 minutes at -40 to -50°, the precipitate dissolved. Stirring was continued for 30 minutes, and the solution was allowed to warm slowly to -20° during one hour. A mixture of acetic acid (12.0 mL) and 1-propanol (20 mL) was added, and all solvents were removed under reduced pressure. The solid residue was triturated with 5% aqueous sodium hydroxide, filtered, washed several times with water and air dried to give 33.5 g of the yellow solid, mp 156-65°. Crystallization from 120 mL of toluene gave 21.3 g of **7** (72%), mp 180-181.5°.

Anal. Calc. for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.80. Found: C, 76.78; H, 7.55.

4-Hydroxy-4-[4'-(3-phenylpropyloxy)biphenyl-4-yl]-1-methylpiperidine (**14**).

To 4-bromo-4'-(3-phenylpropyloxy)biphenyl, **4h**, 73.0 g (0.2 mol) in 800 mL of tetrahydrofuran under nitrogen at -80° was added *via* cannula *n*-butyllithium (100 ml in hexane). A solution of 24.9 g (0.22 mol) of recently distilled 1-methyl-4-piperidone in 800 mL of tetrahydrofuran was added dropwise, and the solution was allowed to warm to room temperature during six hours, whereupon 40 mL of methanol was added. The solvents were removed to give 72.1 g of a yellowish powder, which was heated in 430 mL of boiling toluene, and the slurry was cooled and filtered to give 60 g (75%) of **14**, mp 181-183°.

Anal. Calc. for $C_{27}H_{31}NO_2$: C, 80.76; H, 7.78; N, 3.49. Found: C, 80.30; H, 7.70; N, 3.44.

4-(9,9-Dipropylfluoren-2-yl)-4-hydroxy-1-methylpiperidine (**15**).

A mixture of 2-bromo-9,9-dipropylfluorene (**8**, 32.9 g, 0.094 mol, containing 6% of 2,7-dibromo-9,9-dipropylfluorene **13** [4]) and 100 mL of THF was cooled under nitrogen to below -50° and *n*-butyllithium in hexane (47 mL, 0.1 mol) was added dropwise during 20 minutes, as the temperature was held below -50°. A solution of 1-methyl-4-piperidone (13.5 mL, 0.11 mol, 10% excess) in 25 mL of THF was added during 30 minutes below -50°. The mixture was warmed to -10° during two hours, a solution of acetic acid (12 mL) and 1-propanol (20 mL) was added, and all solvents were removed under reduced pressure. The resulting semi-solid was dissolved in a mixture of methylene chloride and 5% sodium hydroxide solution and extracted 4 times with 30 mL portions of methylene chloride. The solution was dried over sodium carbonate, and the solvent was removed under reduced pressure to yield 37 g of a viscous yellow oil. Crystallization from 60 mL of cyclohexane gave 17.0 g of a white product, mp 137-139°. This product was dissolved in 35 mL of methanol and was diluted with 12 ml of water. The 16.0 g of crystals obtained, mp 140-141°, were recrystallized from the same solvent system to give 14.36 g (42%) of **15**, mp 139.5-140°; 1H nmr: δ 0.63 (s, broad, 10H, $-CH_2CH_2CH_3$), 1.92 (m, 9H, $-CH_2CH_2CH_3$, OH and 3', 5'), 2.30 (s, 3H, $-NCH_3$), 2.57 (t, very broad, J = 8 Hz, 4H, Hs 2', 6'), 7.13-7.43 (m, 3H, Hs 6-8), 7.50-7.83 (m, 4H, Hs 1, 3, 4, 5).

Anal. Calc. for $C_{25}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.44; H, 9.47; N, 3.59.

4-Hydroxy-4-(7-methoxy-9,9-dipropylfluoren-2-yl)-1-methylpiperidine (**16**).

A mixture of 17.95 g (0.05 mol) of bromide **9** [4] and 150 mL of tetrahydrofuran under nitrogen was cooled to -50° and to the homogeneous yellow solution was added *n*-butyllithium (23.8 mL, 0.05 mol) dropwise during 15 minutes while the temperature was maintained below -40°. No precipitate formed during the addition. A solution of 1-methyl-4-piperidone (6.8 mL, 0.055 mol) in 15 mL of tetrahydrofuran was added dropwise during 15 minutes below -40°. The mixture was slowly warmed to -15° during two hours. A mixture of acetic acid (6 mL) and 1-propanol (15 mL) was added dropwise, and all solvents were removed under reduced pressure. The resulting viscous oil was dissolved in a mixture of 5% aqueous sodium hydroxide and methylene chloride, and the aqueous phase was extracted with four times with 30 mL of methylene chloride. The combined organic extract was washed twice with water and once with 30 mL of brine. The solution was dried with anhydrous sodium carbonate, and the solvent was removed to give 20 g of a yellow semi-solid which was triturated with 50 mL of diisopropyl ether and filtered to give 8.0 g of **16**, mp 168-170°. Crystallization from methanol gave the analytical sample, mp 171-172°; ^{1}H nmr: δ 0.68 (s, broad, 10H, $-CH_2CH_2CH_3$), 1.95 (m, 9H, $-CH_2CH_2CH_3$, OH and 3', 5'); 2.37 (s, 3H, $-NCH_3$); 2.67 (t, very broad, *J* = 8 Hz, 4H, Hs 2', 6'); 3.87 (s, 3H, $-OCH_3$); 6.85 (m, 2H, Hs 1, 3); 7.27-7.77 (m, 4H, H's 4, 5, 6, 8).

Anal. Calc. for $C_{26}H_{35}NO_2$.0.15 methanol: C, 78.84; H, 9.01; N, 3.52. Found: C, 78.79; H, 9.37; N, 2.69.

4-Hydroxy-4-[7-(4-methoxyphenyl)-9,9-dipropylfluoren-2-yl]-1-methylpiperidine (**17**).

To 6.5 g (14.9 mmol) of bromide **10** [4] in 40 mL of tetrahydrofuran was added dropwise 6 mL (15 mmol) of *n*-butyllithium with stirring under nitrogen below -40°. The thick mixture was stirred for 30 minutes with continued cooling and 1.9 g of 1-methyl-4-piperidone was added at such a rate that the temperature did not exceed -30°. The temperature was warmed gradually to -10° before 6 mL of methyl alcohol (MeOH) was added. The mixture was concentrated, and the residue was triturated with 100 mL of of 5% sodium hydroxide, filtered, washed with water and dried under an ir lamp. The 6.46 g of crude solid was recrystallized from 180 mL of toluene to give 2.38 g of very light yellow solid, mp 233-235°. The mother liquor on concentration to 40% of its volume gave on cooling 1.5 g of a second crop, mp 230-232°. The combined product was recrystallized twice from toluene (35 mL/g) to give 3.45 g (49%) of **17**, mp 239.5-241°.

Anal. Calcd for $C_{32}H_{39}NO_2$: C, 81.83; H, 8.37; N, 2.98. Found: C, 81.58; H, 8.16; N, 2.82.

4-Hydroxy-4-(6-methoxynaphth-2-yl)-1-methylpiperidine (**18**).

To a dry-ice cooled paste of **11** (30 g, 0.127 mol) in 200 ml of THF was added dropwise *n*-butyllithium (50.6 mL, 0.127 mol) with magnetic stirring under nitrogen. During the addition the temperature of the mixture was kept below -40°. After the reaction mixture was stirred at -60 to-40° for one hour, 15.75 g, (0.139 mol) of 1-methyl-4-piperidone was added at such a rate that the temperature was maintained below -40°. Stirring was continued for half an hour at that temperature and 10 mL of acetic acid in 10 ml of methanol was added as the reaction mixture warmed to -10°. After 5 minutes' stirring, the solvents were removed under reduced pressure. The residue was washed with 10% sodium hydroxide and water, was dried, and was recrystallized from 1.2 L of acetonitrile to give 19.37 g (56%) of a light yellow solid **18**, mp 178.5-180°. A second crop weighed 2.15 g, mp 172-174°.

Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.24; H, 7.80; N, 5.16. Found: C, 75.54; H, 7.97; N, 5.24.

4,4'-Bis(4-hydroxy-1-methyl-4-piperidinyl)biphenyl (**19**).

A solution of 100 g (0.32 mol) of **12**, in 350 mL of tetrahydrofuran at room temperature under nitrogen was cooled to -60° to give a slurry to which *n*-butyllithium (305 ml, 0.67 mol,10% excess) was added dropwise below -50° during an hour. Another 300 ml of THF was added, and after 45 minutes freshly distilled 1-methyl-4-piperidone (82 ml, 0.67 mol) was added dropwise below -50°. The mixture was stirred for an additional 2 hours as it warmed to 15° whereupon 21 mL (0.64 mol) of methanol was added. Solvents were concentrated and the semi-solid was partitioned between methylene chloride and aqueous 30% hydrochloric acid. The organic layer was discarded while the aqueous layer was made basic with 20% NaOH (pH = 11) and extracted 3 times with 80 mL portions of methylene chloride. The combined organic layer was concentrated to a yellowish-white solid which was washed in a sintered glass funnel 4 times with water to give after drying 98 g of crude **19**, mp 209-215°. This was recrystallized three times from a mixture of 60% isopropyl acetate/40% methanol to give 45 g (37%) of **19**, mp 244-246°.

Anal. Calcd. for $C_{24}H_{32}N_2O_2$: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.79; H, 8.47; N, 7.22.

2,7-Bis(4-hydroxy-1-methyl-4-piperidinyl)-9,9-dipropylfluorene (**20**).

A solution of 100 g (0.26 mol) of **13** [4] in 350 mL of tetrahydrofuran was cooled to -60° and 260 mL (0.572 mol, 10% excess) of *n*-butyllithium in hexane was added dropwise at a temperature below -50° during 40 minutes. To the resulting slurry was added an additional 300 mL of tetrahydrofuran. After 30 minutes stirring, 65 mL (0.572 mol, 10% excess) of freshly distilled 1-methyl-4-piperidone was added dropwise below -50°. The reaction was then allowed to warm with stirring for 2 hours before it was quenched by the addition of 17 mL of methanol and subsequently 32 g of acetic acid at 15°. All solvents were removed, and the semi-solid residue was dissolved in a mixture of methylene chloride and aqueous 20% hydrochloric acid (HCl). The organic layer was discarded. The aqueous layer was made basic to pH =11 with 30% NaOH, and was extracted with methylene chloride (3 x 40 mL). The organic layer was dried with anhydrous sodium carbonate and the solvent was concentrated under reduced pressure to give 65 g of a yellowish-white solid which was recrystallized twice from 80% isopropyl acetate/20% methanol to give 37 g (30%) of **20**, mp 229-231°.

Anal. Calcd. for $C_{31}H_{44}N_2O_2$: C, 78.11; H, 9.30; N, 5.88. Found: C, 78.30; H, 9.47; N, 5.78.

4-[4'-(3-Phenylpropyloxy)biphenyl-4-yl]pyridine (**21**).

In 25 mL of diphenyl ether was placed 5.0 g of **14** and 0.6 g of 10% Pd-charcoal. A stream of nitrogen gas was bubbled continuously through the suspension as it was heated to 200° with constant stirring during 52 hours. The mixture was filtered hot through Celite and was filtered again on cooling to give a greyish-green solid. The solid was boiled in 30 mL of butanone and the slurry was allowed to cool and was filtered to give 2.74 g (63%) of a greyish-green **21**, mp 184-186°. Recrystallization of 2.37 g once from 40 mL of 2-methoxyethanol and once from 85 mL of ethyl acetate gave 1.82 g (50%) of **21**, as an off-white solid, mp 188-190°.

Anal. Calc. for $C_{26}H_{23}NO$: C, 85.45; H, 6.36; N, 3.83. Found: C, 85.65; H, 6.14; N, 3.81.

4-(9,9-Dipropylfluoren-2-yl)pyridine (**22**).

A mixture of 10 g of **15**, 0.8 g of 5% palladium on carbon, and 40 mL of diphenylmethane was heated for 51 hours at 240° while nitrogen gas was bubbled through the mixture. The cooled mixture was diluted with methylene chloride and filtered through a bed of Celite. Methylene chloride was removed under reduced pressure, and the diphenylmethane was distilled at 70-110° (0.0l torr) to leave a viscous yellow oil. The residue was dissolved in 10 mL of boiling hexane and crystallized to give 6.80 g (76%) of **22**, mp 91-93°; uv (95% ethanol, c = 2.45 x10^{-5} *M*): 317 nm (33,800); ir (KBr): 3050, 3024, 2952, 2860, 1590, 1450, 1400, 1220, 1152, 990, 810, 782, 740, 700 cm-1; 1H nmr (trifluoroacetic acid): δ 0.75 (s, 10H, -CH2C*H2*C*H3*), 2.20 (t, broad, J = 7 Hz, 4H, -C*H2*CH2CH3), 7.45 (s br, 3H, Hs 6-8), 7.87 (s br, 4H, Hs 1, 3, 4, 5), 8.38 (d, J = 7 Hz, H-3',5'), 8.72 (t, J = 6 Hz, 2H, Hs 2', 6').

Anal. Calc. for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28. Found: C, 87.93; H, 7.88; N, 3.91.

4-(7-Methoxy-9,9-dipropylfluoren-2-yl)pyridine (**23**).

A mixture of **16** (7.0 g), 10% palladium on carbon (0.8 g) and 50 mL of diphenylmethane was heated at 240° for 72 hours while a stream of nitrogen gas was bubbled through the mixture. The cooled mixture was diluted with methylene chloride and filtered through Celite, and was concentrated under reduced pressure. Residual diphenylmethane was distilled at 90-95° (0.01torr) to give a yellow oil which was crystallized from 30 mL of methanol to remove 0.621 g of a brown, non-fluorescent product mp >240° (dec). The parent liquor was concentrated and distilled at 230° (0.01 torr). The distillate was crystallized from 10 ml of hexane to give 2.034 g of **23**, mp 110-112°. Recrystallization from 15 mL of hexane gave 1.49 g of material which assayed 0.8% high for carbon. This material (0.9 g) was used in the synthesis of **23B**. The remainder was crystallized from methanol-water to give analytically pure **23**, mp 110-111°; uv (ethanol, 2.24 x10^{-5} *M*): 329 nm (39,300); ir (KBr): 3060, 3020, 2948, 2860, 1590, 1462, 1400, 1262, 1250, 1030, 812, 680 cm-1; 1H nmr: δ 0.72 (s, broad, 10H,-$CH_2CH_2CH_3$), 1.87 (t, broad J = 7 Hz, 4H, -$CH_2CH_2CH_3$), 3.92 (s, 3H, OCH_3), 6.77-7.17 (m, 2H, H-1; H-3), 7.40-7.80 (m, 6H, Hs 4, 5, 6, 8, 3', 5'), 8.51-8.93 (m, 2H, Hs 2', 6').

Anal. Calcd. for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found: C, 83.69; H, 7.62; N, 3.78.

4-[7-(4-Methoxyphenyl)-9,9-dipropylfluoren-2-yl]pyridine (**24**).

A mixture of **17** (3.0 g, 6.59 mmol), 0.5 g of 10% Pd/C, and 40 mL of diphenylmethane was heated at 220-240° for 18 hours while a stream of nitrogen gas was bubbled through the solution. The reaction mixture was cooled and filtered through Celite/sintered glass, and the catalyst was washed with several portions of methylene chloride. The filtrate was evaporated, and the oil was distilled under reduced pressure (bp 85° at 0.05 torr) to remove most of the diphenylmethane. The residue was triturated with cold acetonitrile, and the solid was filtered, washed with acetonitrile and dried to give 2.5 g of **24**, mp 179-205°. The solid was extracted from a Soxhlet with ethanol for 64 hours. The extract was boiled down to 30 mL and was crystallized to give 1.44 g, mp 177-180°. Recrystallization from acetonitrile gave 1.04 g (36%), of **24** as a yellow solid, mp 180-182°.

Anal. Calcd for $C_{31}H_{31}NO$: C, 85.87; H, 7.21; N, 3.23. Found: C, 86.11; H, 7.21; N, 3.18.

4-(6-Methoxynaphth-2-yl)pyridine (**25**).

A mixture of **18** (19.3 g, 71.1 mmol) and 10% Pd/C in diphenylmethane (150 mL) was heated at 235-245° for 20 hours with stirring provided by a continuous purge of dry nitrogen gas. The reaction mixture was cooled, filtered through Celite in a sintered-glass funnel. The catalyst was washed thoroughly with methylene chloride. The filtrate was distilled under reduced pressure to remove the methylene chloride and the diphenylmethane (bp 82-105°, 0.5 torr). Upon cooling, the residue crystallized during two hours, and the liquid was removed with a pipette. This solid which remained was recrystallized twice from 1,2-dimethoxyethane to give 5.1 g of light yellow solid, mp 153.5-156°. A third recrystallization gave the analytical sample, 3.5 g (21%), mp 155-156.5°. All the mother liquors were combined to give a second crop of 3.3 g, mp 144-149°, of **25**; uv (methanol, 1x10-5 M): 221 nm (44,000), 262 (41,000), 309 (19,000).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.60; H, 5.43; N, 5.83.

4,4'-Bis(4-pyridyl)biphenyl (**26**, 4,4'"-Diazaquaterphenyl).

A stirred slurry of l0 g, (0.026 mol) of **19** and 0.85 g of palladium on carbon in 30 mL of diphenylmethane was purged with nitrogen and heated at reflux (248°) for 72 hours. Methanol (2 mL) was added and the mixture was filtered and washed with 15 mL of methylene chloride in a sintered glass funnel with a celite bed. The volatile solvents were removed, and the diphenylmethane was distilled (bp 70-100° at 0.01 torr). The somewhat viscous residue was triturated in acetonitrile and filtered. The solid, purified by extraction with acetonitrile from a Soxhlet during 48 hours, was collected by filtration to give 5.2 g (53%) of **26**, mp 308-310°.

Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.84; H, 5.03; N, 8.96.

2,7-Bis(4-pyridyl)-9,9-dipropylfluorene (**27**).

A mixture of10 g (0.021 mol) of **20**, 0.85 g of 10% palladium on carbon and 35 mL of diphenylmethane was stirred and refluxed at 248° for 72 hours while nitrogen gas was bubbled continously through the hot mixture. The mixture was cooled, diluted with 20 mL of methylene chloride and was filtered through a bed of Celite in a sintered glass funnel. The filtrate was concentrated and was distilled at 70-100° at 0.01 torr. The 9 g of residual gum was triturated in acetonitrile and filtered. The crude solid was extracted with acetonitrile for 48 hours in a Soxhlet extractor. The solvent was concentrated, and the solid material was washed with acetonitrile and dried to give 6.81 g (80%) of **27**, mp 179-181°. (An earlier sample, mp 171-173° was used for elemental analysis).

Anal. Calcd. for $C_{29}H_{28}N_2$: C, 86.10; H, 6.98; N, 6.92. Found: C, 86.18; H, 6.91; N, 6.73.

4-(4-Chlorophenyl)pyridine (**28**).

Freshly ground magnesium turnings (16.5 g, 0.522 mol, 30% excess) were flame-dried in a flask under nitrogen and allowed to cool to 40°. Tetrahydrofuran (30 mL) was added, the mixture was brought to reflux, and a solution of 100 g (0.522 mol) of 4-bromochlorobenzene in 150 mL of tetrahydrofuran was added at such a rate as to maintain the reflux. After the addition, the reaction was refluxed for an additional two hours. The temperature was decreased to 30°, and salt **5** (28.0 g, 0.186 mol) mixed with PdCl2.dppb (1.0 g, 0.0018 mol) was added in small quantities, while the temperature was maintained below 50°. Stirring was continued for 18 hours, and 100 mL of tetrahydrofuran was added in portions. Methanol 17 mL (1 equivalent) was added and all solvents were removed under reduced pressure. Hydrochloric acid (2 *M*) was added to the oily residue until the pH was 2. The mixture was extracted with methylene chloride (3 x 30 mL) and the extract was discarded. The aqueous layer was treated with portions of saturated sodium bicarbonate solution to pH 8. The mixture was then extracted with methylene chloride (4 x 30 mL), and the organic layer was dried over anhydrous sodium carbonate. The solution was filtered, and the solvent removed under reduced pressure to leave 31.0 g of a crude oil. The oil was distilled to give a forerun of

chlorobenzene (2 g) followed by 24 g of a fraction, bp 90-110° (0.1 mm Hg). This liquid was dissolved in 10% hydrochloric acid upon heating, was filtered hot, was cooled and was basified with a saturated solution of sodium bicarbonate. Crystals, which formed after ice was added, were filtered and washed with water. The dried product (21.2 g) was recrystallized from 70 mL of *n*-hexane to give 18 g (51%) of **28**, mp 70-71°; lit. [18] mp 70-71°; readily sublimes as needles.

4-[4-(6-Methoxynaphth-2-yl)phenyl]pyridine (**29**).

A flask containing 1.02 g (42 mmol) of magnesium was heated to 180° for 15 minutes, was cooled to room temperature, and 100 mL of tetrahydrofuran and 10 g (42 mmol) of **11** were added. Almost all of the magnesium dissolved while the mixture was refluxed with stirring for six hours. The solution was cooled to room temperature and 4 g (21 mmol) of **28**, 350 mg of nickel(II) acetylacetonate and 30 mL of tetrahydrofuran were added. The mixture was refluxed with stirring for 17 hours, was quenched with methanol, and was evaporated to dryness under reduced pressure. The residue was triturated with methanol and filtered to give 9 g of solid. The solid was extracted with methylene chloride (400 mL) in a Soxhlet extractor for 3 days. Evaporation of the extract gave 7.25 g of solid. Extraction of the solid through neutral alumina with boiling cyclohexane in a large Ace-Kau column gave 4.2 g (32 %) of **29**, mp 251-255°

Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.00; H, 5.45; N, 4.35.

4-Bromo-2'-nitrobiphenyl (**30**).

A mixture of 177.4 g (0.89 mol) of 2-nitrobiphenyl, 7.9 g (0.049 mol) of ferric chloride, and 200 mL of water was stirred for one hour before 52 mL (1 mol) of bromine was added dropwise during an hour. The reaction was heated, allowed to cool and was stirred overnight. To the dark brown mixture was added 5.8 g (56.3 mmol) of sodium bisulfite. The mixture was washed with three times with 200 mL-portions of water, once with 5% sodium hydroxide, twice with water, was dried over calcium chloride and evaporated to a yellow oil which crystallized slowly from 75 ml of methanol to give 51.5 g (37%) of **30**, mp 65-6°; lit. [27] mp 63-65°.

2-Bromocarbazole (**31**).

A solution of 27.8 g (0.1 mol) of 4-bromo-2'-nitrobiphenyl **30** and 66.5 mL (0.4 mol) of triethyl phosphite was refluxed for 12 hours under nitrogen. The yellowish-red solution was distilled (68°, 1.25 torr), and the yellow residue was dissolved in 20 mL of acetone, cooled, and filtered to give 15.3 g of crude **31**, mp 234-43°. Recrystallization from 60 mL of butanone gave 6.2 g (39%) of **31**, mp 254-256°; lit. [28] mp 251-252°.

2-Bromo-9-ethylcarbazole (**32**).

To a dark brown solution of 10.61 g, (0.043 mol) of **31** in 120 mL of dimethyl sulfoxide was added 7.26 g (0.0467 mol) of potassium *t*-butoxide under nitrogen was added dropwise during 20 minutes 5.2 mL of ethyl iodide while the temperature was held at 40°. Stirring continued for an additional 1 hour before 140 mL of water was added. This mixture was extracted 4 times with 40 mL-portions of methyl-*t*-butyl ether. The extract was dried with calcium chloride and concentrated to a light yellow liquid which crystallized at 10° to give 11.4 g of **32**. Recrystallization from methyl-*t*-butyl ether gave 10.93 g (92%) of **31**, mp 91.5-92°. Recrystallization from 200 mL of methanol gave 9.17 g (78%) of **32**, mp 92-3°.

Anal. Calcd for $C_{14}H_{12}BrN$: C, 61.33, H, 4.41, N, 5.11. Found: C, 61.33, H, 4.51, N, 5.08.

2-[4-(4-Pyridyl)phenyl]-9-ethylcarbazole (**33**).

Magnesium turnings (0.71 g, 29 mmol) were heated to 110° for 10 minutes, cooled and refluxed with 30 mL of tetrahydrofuran. Solid **32** (8 g, 29 mmol) was added in small quantities during 10 minutes. The magnesium dissolved during two hours reflux and $PdCl_2$-dppb (0.37g, 0.58 mmol) and **28** (4.36g, 0.024 mol), were added in small quantities during 15 minutes while reaction temperature was kept below 45°. Tetrahydrofuran (20 mL) was added, the reaction was stirred for 48 hours before it was quenched with 1 mL of methanol. All solvents were removed, and the gum was acidified with 2 *M* hydrochloric acid and washed with methylene chloride (3x10 mL) . The aqueous layer was made basic with saturated sodium bicarbonate and was extracted with methylene chloride (3x10 ml). The organic layer was dried over sodium carbonate and filtered. The solvent was concentrated to a semi-solid residue which was triturated in ethanol and filtered. Three recrystallizations of the filtrate from toluene gave 0.8 g (10%) of **33**, mp 228-230°.

Anal. Calcd. for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 86.01; H, 5.79; N, 7.89.

4-(4'-Methoxybiphenyl-4-yl)pyridine-*N*-oxide (**34**).

To a solution of 10 g (38.3 mmol) of **3** in 600 mL of chloroform was added 9.5 g of sodium bicarbonate and 23.3 g (115 mmol) of *m*-chloroperoxybenzoic acid, and the mixture was refluxed 15 hours. The suspension was twice extracted with 300 mL of 1 *N* sodium hydroxide, and the chloroform layer was dried with brine followed by magnesium sulfate. The residue after removal of the chloroform crystallized from methanol in three crops to give 6.3 g of **34**, mp 223-225°. Recrystallization gave **34**, mp 224-226°. The identity was confirmed by conversion to **35** and **38**.

2-(4-Methoxyphenyl)-4-(4"-methoxybiphenyl-4-yl)pyridine (**35**).

To a suspension of 3.0 g (10.8 mmol) of **34** in 200 mL of tetrahydrofuran was added 1.36 mL (13.8 mmol) of ethyl chloroformate at 20° with mechanical stirring. After 20 minutes the yellow mixture was cooled to -50° with a dry ice bath. Anisylmagnesium bromide (14.4 mmol: 12 mL of a 1.2 *M* solution in tetrahydrofuran) was added quickly. Most of the solid dissolved as stirring was continued for 5 minutes at -50° and 30 minutes at -70°. The mixture was allowed to warm gradually to room temperature, and 5 mL of methanol was added cautiously. The precipitate was filtered (*ca*. 4 g) and was recrystallized from 45 mL of 2-methoxyethanol to give 1.15 g of **35** as a yellow solid, mp 200-201°. The solid was extracted through a bed of neutral alumina in an Ace-Kau extractor for 24 hours with methylene chloride. The solids obtained on removal of the solvent were recrystallized from 40 mL of 2-methoxyethanol to give 0.74 g (24%) of white **35**, mp 202-203°.

Anal. Calcd. for $C_{25}H_{21}NO_2$ (containing 0.1 mol of 2-methoxyethanol): C, 81.02; H, 5.86; N, 3.73. Found: C, 81.12; H, 5.75; N, 3.70.

2-(2-Hydroxy-5-methylphenyl)-4-(4'-methoxybiphenyl-4-yl)pyridine (**38**).

To a solution of 1.1 g (7.2 mmol) of methoxymethyl *p*-tolyl ether in 20 mL of tetrahydrofuran at -60° was added 2.88 mL (7.2 mmol) of *n*-butyllithium in hexane. The yellow solution was stirred at -70° for 30 minutes, was allowed to warm to 20°, and was transferred *via* cannula under nitrogen to a flask containing 1.33 g (7.2 mmol) of anhydrous magnesium bromide and was stirred for 30 minutes to complete formation of Grignard **36**. In a separate flask, a suspension of 1.00 g (3.6 mmol of **34** in 100 mL of tetrahydrofuran was stirred with 0.41 mL (4.2 mmol) of ethyl chloroformate at 25° for 30 minutes and was cooled to -50°. The solution of **36** was transferred under nitrogen, and the mixture was stirred at -50° for three hours. The solution was allowed to warm to room temperature, quenched with 5 mL of methanol, concentrated to dryness, triturated with hexane and filtered. The 4.4 g of solid obtained was extracted from a Soxhlet with diethyl ether for 16 hours. Concentration of the ether gave a solid which was recrystallzed from 95% ethanol to give 0.15 g, mp 185-191°. Two recrystalizations from small volumes of chloroform gave 25 mg (2%) of **38**, mp 198-199°; 1H nmr (400 MHz, deuteriochloroform): δ 2.26 (s, 3.H), 3.77 (s, 3H), 6.95 (d, J = 9 Hz, 1H, *ortho* to phenol), 7.01 (d, J = 9 Hz, 2H, *ortho* to methoxy), 7.13 (dd, J = 2, 9 Hz, 1H, *ortho* to methyl), 7.46 (dd, J = 2, 5 Hz, 1H, H-5, pyridine), 7.58 (d, J = 9 Hz, 2H, *meta* to methoxy), 7.68 (s, br, 1H, o*rtho* to methyl), 7.70 and 7.75 (two d, J = 9 Hz, 4H, -C6H4-), 8.11, (s, br, 1H, H-3 on pyridine), 8.54 (d, J = 5 Hz, 1H, H-6 on pyridine). and 14.12 (s, v br, 1H, OH).

Anal. Calcd. for $C_{25}H_{21}NO_2$ (containing 0.1 mol of chloroform): C, 79.46; H, 5.81; N, 3.69. Found: C, 79.40; H, 5.65; N, 3.57.

Preparation of Quaternary Salts:

4-(4'-Methoxybiphenyl-4-yl)-1-methylpyridinium Methanesulfonate (**3A**).

To a solution of 3.92 g (15 mmol) of **3** in 40 mL of benzonitrile heated to 105° was added 1.69 mL (2.0 g) of methyl methanesulfonate. A yellow solid, which separated in seconds, redissolved as the temperature was raised to reflux. The solution was immediately allowed to cool to room temperature overnight. It was diluted with 25 mL of toluene, and the yellow solid was filtered and was washed with toluene to give after vacuum drying 5.0 g (90%) of **3A**, mp 258-260°.

Anal. Calc. for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; S, 8.63. Found: C, 64.94; H, 5.61; S, 9.04.

4-(4'-Methoxybiphenyl-4-yl)-1-(3-sulfopropyl)pyridinium Zwitterion (**3B**).

To a warm solution of 7.0 g (26.8 mmol) of **3** in 90 mL of benzonitrile was added 3.9 mL (5.4 g, 44 mmol) of 1,3-propane sultone. The solution was heated to reflux (187°) for 20 minutes, and a precipitate separated. After cooling overnight the solution was filtered and the chartreuse solid was washed with methyl *t*-butyl ether to give 10.44 g (100%) of **3B**, mp 360-361°. Recrystallization of 9.4 g from 15 mL of acetic acid gave 7.01g of **3B**, mp 360-362°. A 1.65 g portion was preadsorbed on Silica Gel and chromatographed on 30 g of Silica Gel. Elution with 25% methanol in methylene chloride gave, after recrystallization from 200 mL of methanol, 1.07 g of **3B**, mp 368-369°; ir (KBr): 3500, 3425, 3030, 2920 w, 1627, 1591, 1487, 1288, 1232, 1175 s, 1042, 1030 sh, 819 cm-1; 1H nmr (trifluoroacetic acid): δ 2.84 (br, pentet, 2H, $NCH_2CH_2CH_2S$), 3.53 (br. t, J = 7 Hz, 2H, $NCH_2CH_2CH_2S$), 4.05 (s, 3H, OCH_3), 4.96 (br. t, J = 7 Hz, 2H, $NCH_2CH_2CH_2S$), 7.20 (d, J = 9 Hz, 2H, H-3", H-5"), 7.72 (d, J = 9 Hz, 2H, H-2", H-6"), 7.90 (s, 4H, Hs 2',3',5',6'), 8.30 (d, J = 7 Hz, 2H, H-3,5), 8.93 (d, J = 7 Hz, 2H, H-2,6).

Anal. Calc. for $C_{21}H_{21}NO_4S$: C, 65.77; H, 5.52; S, 8.36. Found: C, 66.03; H, 5.70; S, 8.49.

4-(4'-Methoxybiphenyl-4-yl)-1-(3-sulfobutyl)pyridinium Zwitterion (**3C**).

This was prepared in the manner of the sulfopropyl analog **3B**. The free base **3** (1.6 g, 0.0061 mol) and 1,4-butane sultone (1.04 g, 0.78 mL, 0.00763 mol) in 35 mL of benzonitrile were boiled under reflux for 30 minutes. The mixture at 20° was filtered, the product was washed with toluene and dried to give 2.06 g (85%) of lemon-yellow solid, mp 359-360° (dec). uv (ethanol, 2.4 x10-5 M) 203 nm (ε = 36,000); 248 (18,000); 360 (28,000).

Anal. Calc. for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52. Found: C, 66.51; H, 5.66; N, 3.56.

4-(9,9-Dipropylfluoren-2-yl)-1-(3-sulfopropyl)pyridinium Zwitterion (**22B**).

To a warm solution of 1.0 g (3.07 mmol) of **22** in 10 mL of benzonitrile was added 0.47 g (3.83 mmol) of 1,3-propane sultone. The solution was heated to reflux for 15 minutes and allowed to cool. Filtration of the suspension after two days gave after washing twice with toluene and drying (110°, 30 torr, 3 hours) gave 1.34 g (98%) of **22B**, mp 274-276.5°; uv (methanol): 361 nm (33,000); ir (KBr): 3400 br, 3100 sh, 3007, 2950, 2920, 2862, 1627, 1604, 1510, 1450, 1423, 1280, 1180 s, br, 1032, 861, 832, 787, 769, 740 cm-1.

Anal. Calc. for $C_{27}H_{31}NO_3S$: C, 72.13; H, 6.95; S, 7.13. Found: C, 71.95; H, 6.72; S, 7.40.

4-(7-Methoxy-9,9-dipropylfluoren-2-yl)-1-sulfopropylpyridine Zwitterion (**23B**).

By the method for **22B**, 0.90 g (2.5 mmol) of **23** was converted to 1.21 g of **23B**, mp 260-270°. This was recrystallized from 20 mL of 1:1 benzonitrile/dibutyl ether to give 0.89 g (74%) of **23B**, mp 267-269° which showed green fluorescence in chloroform or methanol; uv (methanol) 385 nm (33,000); ir (KBr): 3020 br, 3040, 2960, 2930, 2880, 2850 sh, 1625 sh, 1600, 1580 sh, 1518, 1460, 1425 sh, 1345, 1310 sh, 1180 s, br, 1100, 1035 s, 1005, 868, 817, 781, 755, 728 cm-1; 1H nmr (trifluoroacetic acid): δ 0.7 (s, broad, 10H,-$CH_2CH_2CH_3$), 2.18 (m, 4H, -$CH_2CH_2CH_3$), 2.82 (br, pentet, 2H, $NCH_2CH_2CH_2S$), 3.53 (br. t, J = 7 Hz, 2H, $NCH_2CH_2CH_2S$), 4.13 (s, 3H, OCH_3), 4.93 (br. t, J = 7 Hz, 2H, $NCH_2CH_2CH_2S$), 7.13 (m, 2H, H-6'; H-8'), 7.90 (d, J = 9 Hz, 1H, H-5'), 7.95 (s, 3H, Hs 1', 3',4'), 8.30 (d, J = 7 Hz, 2H, H-3,5), 8.60 (d, J = 7 Hz, 2H, H-2,6).

Anal. Calc. for $C_{28}H_{33}NO_4S$: C, 70.11; H, 6.77; S, 6.52. Found: C, 68.61; H, 6.82; S, 6.87.

4-[7-(4-Methoxyphenyl)-9,9-dipropylfluoren-2-yl]-1-sulfopropylpyridinium Zwitterion (**24B).**

To a hot solution of 0.6 g (1.38 mmol) of **24** in 5 mL of benzonitrile was added 0.5 g (4.0 mmol) of 1,3-propane sultone. The mixture was stirred at 180° for 30 minutes and allowed to cool slowly. The precipitate was filtered and washed with acetonitrile to give 400 mg of **24B**, mp 314-316°. The filtrate was

diluted with 25 mL of methyl *t*-butyl ether and an additional 400 mg of yellow precipitate was obtained. The combined solids on recrystallization from 20 mL of absolute ethanol gave 0.63 g of **24B**, mp 320.5-321° (dec).

Anal. Calcd for $C_{34}H_{37}NO_4S$: C, 73.48; H, 6.71; N, 2.52. Found: C, 73.22; H, 6.77; N, 2.39.

4-(6-Methoxynaphth-2-yl)-1-methylpyridinium methanesulfonate (**25A**).

To a solution of **25** (1.5 g, 6.38 mmol) in 17 mL of acetonitrile was added 2.1 g (19.1 mmol) methyl methanesulfonate. The mixture was refluxed for 46 hours as the disappearance of the **25** was monitored by tlc (1,2-dimethoxyethane/Silica Gel). The addition of toluene to the hot solution caused the separation of a gum which was induced to crystallize. The solid was collected by filtration and washed with toluene to give 1.2 g, mp 184-186°. Recrystallization from 10 mL of acetonitrile gave 0.63 g of yellow solid, **25A**, mp 194-195°; uv (MeOH, 5x10-5 *M*): 225 nm (42,000), 259 (16,000), 286 (17,000), 367 (20,000).

Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06. Found: C, 62.01; H, 5.75; N, 3.92.

4-(6-Methoxynaphth-2-yl)-1-(3-sulfopropyl)pyridinium Zwitterion (**25B**).

To a hot solution of **25** (1.5 g, 6.38 mmol) in 5 mL of benzonitrile was added 1.2 g (9.6 mmol) of 1,3-propane sultone. The solution was heated to 180° for 10 minutes and was allowed to cool slowly. The solid which separated was collected by filtration, was washed with methyl *t*-butyl ether, and was recrystallized from 200 mL of absolute ethanol to give 1.90 g (83 %) of **25B** as a yellow solid, mp 295-297° (dec); uv (methanol, 5x10-5 *M*): 225 nm (40,000), 260 (15,000), 289 (15,000), 370 (20,000).

Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92. Found: C, 64.44; H, 5.61; N, 3.89.

4,4'-Bis(1-methyl-4-pyridinium)biphenyl Dimesylate (**26A**).

To a solution of 1.0 g (3.2 mmol) of **26** in 20 mL of benzonitrile at 140° was added 0.7 g of methyl methanesulfonate. A yellow solid immediately choked the stirring and 10 mL of benzonitrile was added and the reaction mixture was heated for another 15 minutes before it was slowly cooled to room temperature. The precipitate was filtered, washed with toluene, and then dried at 100°/20 torr for 30 hours to give 1.63 g (84%) of **26A**, mp 323-325° (dec). uv (methanol) 344 nm (52,600). Fluorescence ca. 420 nm. Quantum efficiency 1.0 [24].

Anal. Calcd. for $C_{26}H_{28}N_2O_6S_2$: C, 59.07; H, 5.34; N, 5.30. Found: C, 59.35; H, 5.40; N, 5.37.

4,4'-Bis(1-sulfopropyl-4-pyridinium)biphenyl (**26B**).

To 1.0 g (3.2 mmol) of **26** at 130° in 30 mL of benzonitrile was added 0.78 g (6.4 mmol) of 1,3-propane sultone. Heating was continued for 15 minutes to digest the yellowish crystals which formed instantly. The crystals, were filtered, washed with 25 mL of toluene, and dried (100°/20 torr/42 hours) to give 1.68 g (95%) of **26B** mp >400°. A 0.55 g portion of the yellow solid was placed in a Soxhlet and extracted with boiling acetic acid for 36 hours. The short, off-white needles suspended in the hot solution were collected by filtration to give 0.28 g (44%) of **26B** as the sesquisolvate, browns 370-400°, sublimes partially 410-430° but does not melt to 490°.

Anal. Calcd. for $C_{28}H_{28}N_2O_6S_2.1.5\ CH_3CO_2H$: C, 57.93; H, 5.33; N, 4.36. Found: C, 58.08; H, 5.48; N, 4.61.

2,7-Bis(1-methyl-4-pyridinium)-9,9-dipropylfluorene Dimethanesulfonate (**27A**).

To a refluxing solution of 1.0 g (2.5 mmol) of **27** in 25 mL of acetonitrile was added 0.6 g (5.5 mmol) of methyl methanesulfonate. Refluxing was maintained for an additional 8 hours before the mixture was cooled, concentrated to dryness, and crystallized from 10 mL of toluene to give 1.47 g (94%) of **27A**, mp 324-325°. uv (methanol) 377 nm. Fluorescence (methanol) 445 nm. Quantum efficiency 0.82 [24].

Anal. Calcd. for $C_{33}H_{40}N_2O_6S_2$: C, 63.50; H, 6.46; N, 4.49. Found: C, 63.53; H, 6.51; N, 4.39.

9,9-Dipropyl-2,7-bis(1-sulfopropyl-4-pyridinium)fluorene (**27B**).

A slurry of 1.0 g (2.5 mmol) of **27** in 15 mL of benzonitrile was heated to 140° and 0.67 g (5.5 mmol) of melted 1,3-propane sultone was added and the mixture was heated to reflux for 15 minutes. The yellowish crystals which formed immediately were allowed to cool slowly to room temperature, were filtered, and were washed with 20 mL of toluene. The crystals were dried at 100°/26 torr to give 1.60 g (99%) of **27B**, mp 359-361° (dec). uv (methanol) 378 nm (58,000).

Anal. Calcd. for $C_{35}H_{40}N_2O_6S_2$: C, 64.79; H, 6.21; N, 4.32. Found: C, 64.68; H, 6.12; N, 4.16.

2-(1-Decyl-4-pyridinium)-7-(4-pyridyl)-9,9-dipropylfluorene Bromide (**27C**).

To a refluxing solution of 0.20 g, (0.5 mmol, mp 171-173°) of **27** in 12 mL of acetonitrile was added 0.122 g, (0.55 mmol) of 1-bromodecane, and the solution was heated at reflux for 8 hours while the color gradually changed from yellowish-green to light yellow. The solvent was removed under reduced pressure and the residue was crystallized from 2 mL of acetonitrile to give 0.3 g of a yellow product, mp 184-189°. Recrystallization from 1.5 mL of acetonitrile gave 0.28 g (90%) of **27C**, mp 193-195°.

Anal. Calcd. for $C_{39}H_{49}N_2Br$: C, 74.86; H, 7.89; N, 4.48. Found: C, 74.28; H, 7.78; N, 4.28.

4-[4-(6-Methoxynaphth-2-yl)phenyl]-1-sulfopropylpyridinium Zwitterion (**29B**).

A mixture of 1.0 g (3.21 mmol) of **29** and 25 mL of benzonitrile was heated with mechanical stirring. After the solid dissolved 1,3-propane sultone (1.0 g, 8.1 mmol) was added. A yellow precipitate immediately separated from the hot solution, and the mixture was stirred for 1 hour at *ca*. 80°. After standing at room temperature overnight, the mixture was filtered. The solid was washed with acetonitrile and diisopropyl ether to give 1.4 g of **29B** as a yellow solid, mp. 366-370° dec). A 1.17 g portion was recrystallized from 400 mL of dimethylformamide with a hot filtration to give on cooling 0.86 g (62%) of **29B**, mp 268-270°.

Anal. Calcd for $C_{25}H_{23}NO_4S$: C, 69.26; H, 5.35; N, 3.23. Found: C, 69.40, H, 5.37; N, 3.47.

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