SYNTHESES OF 2-AZAFLUORENONES FROM 3-SUBSTITUTED 4-ARYLPYRIDINES

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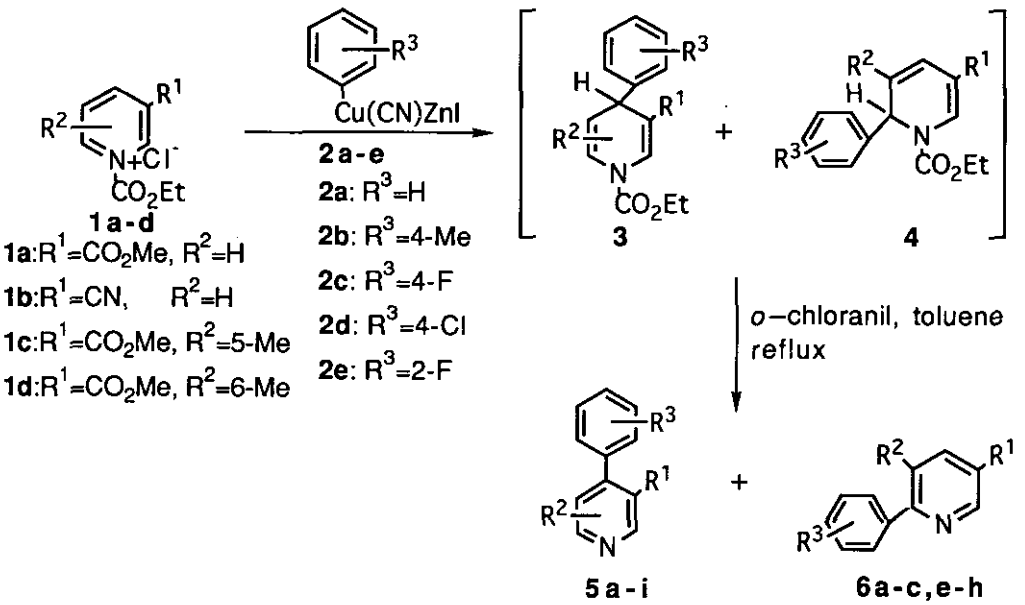
Abstract--*3-Substituted 4-arylpyridines* (**5a-i**) were synthesized in good yields by reaction of mixed copper, zinc aryl organometallics (**2a-e**) with 1-ethoxycarbonyl-pyridinium chlorides (**1a-d**) followed by *o-chloranil* oxidation under reflux in toluene. The 4-arylpyridines (**5a-i**) are obtained predominantly. Having compounds (**5a-i**) in hand, a convenient method was developed for the synthesis of 2-azafluorenones (**7a-f**) by using cyclization of 4-arylpyridines (**5a-i**) with polyphosphoric acid.

Fluorenones and their derivatives have been known to be good antiviral agents[1] and aldose reductase inhibitors,[2] respectively; Therefore azafluorenones derivatives may as well possess interesting biological properties. Azafluorenones compounds are structurally related to a significant class of alkaloids such as onychines.[3] The regioselective synthesis of 4-aryl-pyridines[4,5] was already reported using *N*-acylpyridinium salts and Grignard reagents in the presence of copper(I) iodide.[6] The preparation of several tricyclic pyridines such as 2-azafluorenone (9*H*-indeno[2,1-*c*]pyridin-9-one) was also reported, based on this method.[7] Prostakov *et al.*[8] found that the

cyclization of 4-phenylpyridine-3-carboxylic acid in concentrated sulfuric acid at 100 °C yields 2-azafluorenone. Fuson and Miller[9] prepared 2-azafluorenone from 3-mesitoyl-4-phenylpyridine or 3-duroyl-4-phenylpyridine by treatment with polyphosphoric acid (PPA). Abramovitch[10] investigated the decomposition of the diazonium salt from 3-(*o*-aminobenzoyl)pyridine under various conditions. The formation of 2-azafluorenone and other products occurred *via* a radical process in the copper-catalyzed reaction. Recently we also found that mixed copper, zinc benzylic organometallics can be added to pyridinium salts to obtain functionalized 4-benzylpyridines in a regio- and chemoselective

Scheme I



5a: R^1=CO_2Me, R^2=H, R^3=H **6a**: R^1=CO_2Me, R^2=H, R^3=H
5b: R^1=CN, R^2=H, R^3=H **6b**: R^1=CN, R^2=H, R^3=H
5c: R^1=CO_2Me, R^2=5-Me, R^3=H **6c**: R^1=CO_2Me, R^2=5-Me, R^3=H
5d: R^1=CO_2Me, R^2=6-Me, R^3=H **6e**: R^1=CO_2Me, R^2=H, R^3=4'-Me
5e: R^1=CO_2Me, R^2=H, R^3=4'-Me **6f**: R^1=CO_2Me, R^2=H, R^3=4'-F
5f: R^1=CO_2Me, R^2=H, R^3=4'-F **6g**: R^1=CN, R^2=H, R^3=4'-F
5g: R^1=CN, R^2=H, R^3=4'-F **6h**: R^1=CO_2Me, R^2=H, R^3=4'-Cl
5h: R^1=CO_2Me, R^2=H, R^3=4'-Cl
5i: R^1=CO_2Me, R^2=H, R^3=2'-F

manner.[11] Here we wish to report the synthesis of 2-azafluorenones (**7a-f**) from substituted 4-arylpyridines (**5a-i**), which were synthesized in good yields by reaction of mixed zinc aryl organometallics (**2**)[12] with 1-ethoxycarbonyl-pyridinium chlorides (**1a-d**) followed by *o*-chloranil oxidation (Scheme I).

The starting materials, 3-substituted 4-arylpyridines (**5a-i**), were synthesized by the addition of mixed copper, zinc aryl nucleophiles to pyridinium salts. The mixed copper, zinc aryl organometallics (**2a-e**) were prepared by zinc metal insertion, followed by transmetallation with copper. Treatment of aforementioned nucleophiles with pyridinium salts (**1a**) or (**1b**) was conducted at -78 °C under an inert atmosphere. The intermediate 1,4-dihydropyridines (**3**) or 1,6-dihydropyridines (**4**), were found to be temporarily stable in air at room temperature, they can be oxidized by *o*-chloranil[13] in refluxing toluene. The highly regioselective preparation of 4-arylpyridines (**5a-i**) and **6**-arylpyridines (**6a-c,e-h**) was accomplished by the reactions of mixed copper, zinc aryl nucleophiles (**2a-e**) having nitriles and methyl ester functionality at C_3 position with various pyridinium salts (**1a-d**). It should be noted that the reactions of **1a-d** with **2a-e** gave a mixture of the products (**5a-i**) and

Table 1. Synthesis of 4-Arylpyridines (**5a-i**) and 6-Arylpyridines (**6a-c,e-h**)

1	2	Yield of 5, 6 (%)[a]	Ratio of 5 / 6
1a	2a	**5a**(61) **6a**(24)	2.5
1b	2a	**5b**(56) **6b**(19)	3.0
1c	2a	**5c**(47) **6c**(16)	2.9
1d	2a	**5d**(41)	
1a	2b	**5e**(59) **6e**(18)	3.3
1a	2c	**5f**(56) **6f**(14)	4.0
1b	2c	**5g**(40) **6g**(10)	4.0
1a	2d	**5h**(43) **6h**(8)	5.4
1a	2e	**5i**(63)	

[a]isolated yields.

(**6a-c,e-h**) in favor of 4-arylpyridine derivatives (**5a-i**) and the ratios were shown in Table I. It is not clear that compound (**5d**) and (**5i**) were the exclusively formed products from the reactions between **1d** and **2a** or **1a** and **2e**, respectively. It should be mentioned that the 2-arylpyridine derivatives were not obtained in the above reactions. Furthermore, there was no reaction between the functional groups of pyridinium salts and the nuclophiles, which indicate the high chemoselectivity of such nucleophiles toward the pyridinium salts. Having established a new and convenient procedure for the preparation of functionalized 4-arylpyridines (**5a-i**), it was decided to prepare 2-azafluorenone, which might have interesting biological activies.[14] Compounds (**5a-i**) were cyclized in hot PPA to give substituted 2-azafluorenones (**7a-f**) in 40-95% (Table 2 and Scheme II). Methyl ester (**5a**) and nitrile (**5b**) gave **7a** in a

Table 2. Reaction Conditions of **5a-i** with PPA to Form **7a-f** and **8a**

5	Temp (°C)	Time (h)	Yield of 7, 8 (%)[a]
5a	210	4	**7a**(86)
5b	210	10	**7a**(85)
5c	210	3	**7b**(95)
5d	210	2	**7c**(81)
5e	210	2	**7d**(89)
5f	200	8	**7e**(53)
5g	210	6	**7e**(40)
5h	200	2	**7f**(48)
5i	180	2	**8a**(78)

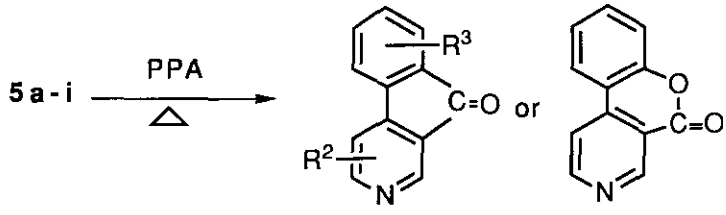
[a]isolated yields.

yield of 86% and 85%, respectively. Similarly **5f** and **5g** both afforded **7e** in a yield of 53% and 40%, respectively. It is interesting to note that compound (**5i**) did not give the corresponding 2-azafluorenone but instead 5*H*[1]-benzopyrano[3,4-*c*]pyridin-5-one[7,15] (**8a**) (78%) was obtained.

In summary, we have developed a new and convenient method to synthesize 3-substituted 4-arylpyridines (**5a-i**) by mixed copper, zinc aryl organometallics

(**2a-e**) with 1-ethoxycarbonylpyridinium chlorides (**1a-d**) followed by *o*-chloranil oxidation. The 4-arylpyridines (**5a-i**) were obtained predominantly. The present results also disclose a convenient method for the synthesis of 2-azafluorenones (**7a-f**) from 4-arylpyridines (**5a-i**) by its cyclization with PPA. When the aryl moiety is substituted at C_2 with a fluoro function such as **5i** the cyclization product is 5*H*[1]benzopyrano[3,4-*c*]pyridin-5-one (**8a**).

Scheme II



7a-f **8a**

7a: R^2=H, R^3=H
7b: R^2=4-Me, R^3=H
7c: R^2=3-Me, R^3=H
7d: R^2=H, R^3=7-Me
7e: R^2=H, R^3=7-F
7f: R^2=H, R^3=7-Cl

EXPERIMENTAL

Melting points are uncorrocted. The ^{1}H-nmr spectra were recorded on Bruker AC 200 and MSL 200 spectrometers. The ms spectra were obtained by using a VG 7-250 GC-MS system at 70 eV. The ir spectra were measured with a Perkin-Elmer 882 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyzer. All anhydrous solvents were freshly distilled before use.

General Procedure for the Synthesis of 4- and 6-arylpyridines (**5a-i**) and (**6a-f**).

Synthesis of Methyl 4-Phenylnicotinate[16] (**5a**) and Methyl 6-Phenylnicotinate[16] (**6a**):

To a solution of iodobenzene **2a** (4.08 g, 20 mmol) in 30 ml of DMF was slowly added at 75°C activated zinc (1.31 g, 22 mmol). After this solution was stirred at 75°C under nitrogen for 20 h, it was then added to a 30 ml of THF soution containing CuCN (1.79 g, 20 mmol) and LiCl (1.78 g, 42 mmol) at -70°C. After being warmed up to 0°C for 15 min, the reaction mixture was cooled down to -30°C again. The solution was added to a solution of pyridinium chloride (**1**) [prepared from 10 mmol (1.09 g) of ethyl chloroformate, 10 mmol of 3-substituted pyridine, 40 ml of THF at -55°C for 30 min) at -55°C within 1h. The reaction mixure was quenched by the addition of 5% NH_4OH solution (50 ml). After evaporation of THF, the residue was extracted with dichoromethane (3 x 80 ml), the organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was heated over *o*-chloranil (2.95 g, 12 mmol) in toluene (20 ml) at 130°C for 3h. The mixture was cooled and neutralized with a 10 % NaOH, then extracted with dichloromethane (3 x 50 ml), dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude product, which was purified by column chromatography (ethyl acetate / hexane 1:3) and then bulb to bulb distillation to give the corresponding **5a** (2.60 g, 61%) and **6a** (1.02 g, 24%). **5a:** Colorless oil[16]; bp 193-198°C/3 torr. **6a**: White solid; mp 109-111°C (CH_2Cl_2)(lit.,[16] 113-114 °C). Compounds (**5b-i** and **6b,c,e-h**) were similarly prepared.

3-Cyano-4-phenylpyridine (**5b**) and 3-Cyano-6-phenylpyridine (**6b**)

5b: Yield 56 %; Pale yellow solid; mp 65.5-66.5°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 8.95 (1H, d, J = 0.5 Hz, pyridyl H-2), 8.81 (1H, d, J = 5.2 Hz, pyridyl H-6), 7.66-7.52 (5H, m, aryl 5H), 7.48 (1H, d, J = 5.2 Hz, pyridyl H-5); ir (cm^{-1}) ($CHCl_3$): 3087, 3037, 2993, 2228 (C≡N), 1571, 1531, 1463; ms m/z: 180 (M^+, 100), 154 (20), 153 (23), 126 (10), 77 (12); Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.48; N, 15.54. Found: C, 79.84; H, 4.24; N, 15.45. **6b**: Yield 19%; White solid;

mp 84-85°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 8.83 (1H, d, J = 1.7 Hz, pyridyl H-2), 7.96 - 7.86 (3H, m, pyridyl H-4 and aryl 2H), 7.73 (1H, d, J = 7.8 Hz, pyridyl H-5), 7.45 - 7.38 (3H, m, aryl 3H); ir (cm^{-1}) ($CHCl_3$): 3047, 2928, 2232 (C≡N), 1579, 1436; ms m/z: 180 (M^+, 100), 152 (12), 103 (6), 90 (6). Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.48; N, 15.54. Found: C, 79.76; H, 4.36; N, 15.35.

Methy 5-methyl-4-phenylnicotinate (**5c**) and Methyl 5-Methyl-6-phenyl-*nicotinate* (**6c**)

5c: Yield 47 %; White solid; mp 49-50°C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$): δ 8.80 (1H, s, pyridyl H-2), 8.49 (1H, s, pyridyl H-6), 7.32 - 7.28 (3H, m, aryl 3H), 7.04 - 7.00 (2H, m, aryl 2H), 3.48 (3H, s, CO_2Me), 1.99 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 3035, 3005, 2954, 1719 (C=O), 1644, 1617, 1575 , 1545, 1437; ms m/z: 227 (M^+, 71), 212 (7), 196 (100), 180 (10), 167(53), 139 (14), 115 (16); Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.76; H, 5.92; N, 5.93. **6c**: Yield 16 %; White solid; mp 55-56°C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$): δ 9.02 (1H, d, J = 1.7 Hz, pyridyl H-2), 8.11 (1H, d, J = 1.7 Hz, pyridyl H-4), 7.49 - 7.33 (5H, m, aryl 5H), 3.88 (3H, s, CO_2Me), 2.33 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 3058, 3028, 2954, 1781, 1728 (C=O), 1596, 1541, 1423, 1399; ms m/z: 227 (M^+, 52), 212 (100), 196 (23), 166 (18), 153 (19), 141 (14), 129 (10), 106 (8); Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.72; H, 5.81; N, 5.97.

Methyl 4-(4'-phenyl)-6-methylnicotinate (**5d**)

Yield 41%; White solid; mp 72-73°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 8.86 (1H, s, pyridyl H-2), 7.34-7.31 (3H, m, aryl 3H), 7.23-7.18 (2H, m, aryl 2H), 7.06 (1H, s, pyridyl H-5), 3.60 (3H, s, CO_2Me), 2.54 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 3051, 2949, 1712 (C=O), 1579, 1521, 1423; ms m/z: 227 (M^+, 74), 196 (100), 182 (4), 168 (16), 141 (8); Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16 Found: C, 73.77; H, 5.84; N, 6.31.

Methyl 4-(4'-tolyl)nicotinate (**5e**) and Methyl 6-(4'-tolyl)*nicotinate* (**6e**)

5e: Yield 59%; White solid; mp 61-62 °C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$): δ 8.92 (1H, s, pyridyl H-2), 8.62 (1H, d, J = 4.8 Hz, pyridyl H-6), 7.22 (1H, d, J = 4.8 Hz, pyridyl

H-5), 7.21-7.13 (4H, m, aryl 4H), 3.66 (3H, s, CO_2Me), 2.33 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 3001, 2955, 1723 (C=O), 1588, 1478, 1433, 1404, 1288, 1202, 1112, 1052, 817; ms m/z: 227 (M^+, 92), 196 (100), 168 (28); Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.71; H, 5.41; N, 5.89. **6e**: Yield 18%; White solid; mp 114-115°C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$): δ 9.17 (1H, d, J = 2.1 Hz, pyridyl H-2), 8.23 (1H, dd, J = 2.1, 8.3 Hz, pyridyl H-4), 7.87 (2H,dd, J = 2.0, 8.2 Hz, aryl 2H), 7.78 (1H, d, J = 8.3 Hz, pyridyl H-5), 7.18 (2H, dd, J = 2.0, 8.2 Hz, aryl 2H), 3.88 (3H, s, CO_2Me), 2.33 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 2986, 1717 (C=O), 1599, 1455, 1415; ms m/z: 227 (M^+, 100), 196 (60), 168 (17); Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.70; H, 5.60; N, 5.98.

Methyl 4-(4'-fluorophenyl)nicotinate (**5f**) and Methyl 6-(4'-fluorophenyl)-nicotinate (**6f**)

5f: Yield 56%, White solid; mp 90-92°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 9.05 (1H, s, pyridyl H-2), 8.73 (1H, d, J = 4.7 Hz, pyridyl H-6), 7.35-7.27 (3H, m, pyridyl H-5 and aryl 2H), 7.19-7.10 (2H, dd, J = 2.1, 8.3 Hz, aryl 2H), 3.70 (3H, s, CO_2Me); ir (cm^{-1}) ($CHCl_3$): 3038, 2992, 2966, 1726 (C=O), 1608, 1589, 1538, 1478, 1287, 1207, 1115, 833; ms m/z: 231 (M^+, 96), 200 (100), 172 (35), 145 (27), 125 (10); Anal. Calcd for $C_{13}H_{10}NO_2F$: C, 67.53; H, 4.36; N, 6.06. Found: C, 67.16; H, 4.30; N, 5.90. **6f**: Yield 14%; White solid; mp 123-124°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 9.26 (1H, s, pyridyl H-2), 8.34 (1H, d, J = 8.3 Hz, pyridyl H-4), 8.06 (2H, dd, J = 2.0, 8.2 Hz, aryl 2H), 7.76 (1H, d, J = 8.3 Hz, pyridyl H-5), 7.21 (2H, dd, J = 2.0, 8.2 Hz, aryl 2H), 3.97 (3H, s, CO_2Me); ir (cm^{-1}) ($CHCl_3$): 3002, 2953, 1774, 1721 (C=O), 1594, 1474, 1435, 1289, 1157, 1033, 837; ms m/z: 231 (M^+, 58), 218 (40), 200 (65), 145 (21), 123 (100), 116 (57), 95 (52), 83 (32); hrms Calcd for $C_{13}H_{10}NO_2F$: 231.0696; Found: 231.0688.

3-Cyano-4-(4'-fluorophenyl)pyridine (**5g**) and 3-Cyano-6-(4'-fluorophenyl)-pyridine (**6g**)

5g: Yield 40%; White solid; mp 128-130°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 8.96 (1H, s, pyridyl H-2), 8.82 (1H, d, J = 5.4 Hz, pyridyl H-6), 7.63 (2H, dd, J = 2.0, 8.0 Hz, aryl 2H), 7.45 (1H, d, J = 5.4 Hz, pyridyl H-5), 7.26 (2H, dd, J = 2.0, 8.0 Hz, aryl 2H); ir (cm^{-1}) ($CHCl_3$): 2993, 2231 (C≡N), 1646, 1601, 1583, 1509, 1476, 1397, 1201; ms m/z: 198 (M^+, 100), 171 (19), 145 (10), 120 (8), 99 (8), 75 (8); Anal. Calcd for $C_{12}H_7N_2F$: C, 72.72; H, 3.56; N, 14.13. Found: C, 72.57; H, 3.75; N, 13.94. **6g**: yield 10%; White solid; mp 145-146°C (CH_2Cl_2/hexane); ^{1}H-nmr ($CDCl_3$): δ 8.92 (1H, d, J = 2.2 Hz, pyridyl H-2), 8.09-7.98 (3H, m, pyridyl H-5 and aryl 2H), 7.79 (1H, dd, J = 2.2, 8.4 Hz, pyridyl H-4), 7.20 (2H, dd, J = 2.0, 8.0 Hz, aryl 2H); ir (cm^{-1}) ($CHCl_3$): 3014, 2233 (C≡N), 1651, 1589, 1504, 1472, 1374, 1297, 1204; ms m/z: 198 (M^+,100), 171 (13), 138 (14), 123 (45), 109 (30), 95 (21), 75 (13); hrms Calcd for $C_{12}H_7N_2F$: 198.0593; Found: 198.0585.

Methyl 4-(4'-chlorophenyl)nicotinate (**5h**) and Methyl 6-(4'-chlorophenyl)-nicotinate (**6h**)

5h: Yield 43%, White solid; mp 65-66°C (hexane); ^{1}H-nmr ($CDCl_3$): δ 9.06 (1H, s, pyridyl H-2), 8.73 (1H, d, J = 5.1 Hz, pyridyl H-6), 7.41 (2H, dd, J = 2.2, 8.4 Hz, aryl 2H), 7.29-7.23 (3H, m, pyridyl H-5 and aryl 2H), 3.75 (3H, s, CO_2Me); ir (cm^{-1}) ($CHCl_3$): 2985, 2955, 1723 (C=O), 1585, 1473, 1432, 1287, 1204, 1115, 1091, 1011, 824; ms m/z: 249 (M^++2, 24), 247 (M^+, 76), 216 (100), 188 (33), 139 (25), 126 (23); Anal. Calcd for $C_{13}H_{10}NO_2Cl$: C, 63.04; H, 4.07; N, 5.66; Found: C, 62.81; H, 3.88; N, 5.44. **6h**: Yield 8%, White solid; mp 113-115°C (hexane); ^{1}H-nmr ($CDCl_3$): δ 9.26 (1H, d, J = 2.1 Hz, pyridyl H-2), 8.34 (1H, dd, J = 2.1, 8.3 Hz, pyridyl H-4), 7.99 (2H, dd, J = 2.4, 8.6 Hz, aryl 2H), 7.77 (1H, d, J = 8.3 Hz, pyridyl H-5), 7.47 (2H, dd, J = 2.4, 8.6 Hz, aryl 2H), 3.97 (3H, s, CO_2Me); ir (cm^{-1}) ($CHCl_3$): 2990, 2955, 1771, 1720 (C=O), 1591, 1426, 1283, 1200, 1121, 1095, 1010; ms m/z: 249 (M^++2, 13), 247 (M^+, 40), 235 (100), 227 (45), 216 (32), 198 (33), 168 (72), 125 (71); hrms Calcd for $C_{13}H_{10}NO_2Cl$: 247.0400; Found: 247.0395.

Methyl 4-(2'-fluorophenyl)nicotinate (**5i**)

Yield 63%; Colorless oil; bp 215-217°C/4 torr; ^{1}H-nmr ($CDCl_3$): δ 9.16 (1H, s, pyridyl H-2), 8.78 (1H, d, J = 5.1 Hz, pyridyl H-6), 7.44-7.08 (5H, m, pyridyl H-5 and aryl 4H), 3.77 (3H, s, CO_2Me); ir (cm^{-1}) ($CHCl_3$): 3044, 3004, 2951, 1722 (C=O), 1614, 1585, 1538, 1476, 1433, 1272, 1116, 832, 758; ms m/z: 231 (M^+, 100), 212 (10), 200 (94), 172 (42), 145 (23), 125 (20); hrms Calcd for $C_{13}H_{10}NO_2F$: 231.0696; Found: 231.0705.

General Procedure for the Synthesis of 2-Azafluorenone (**7a-f**) from 4-arylpyridines (**5a-i**)

Synthesis of 2-azafluorenone (9*H*-indeno[2,1-*c*]pyridin-9-one)[7] (**7a**) from **5a**: A mixture of **5a** (0.30 g, 1.4 mmol) and polyphosphoric acid (7.00 g) was heated at 210°C for 4 h. It was cooled to 0°C, quenched by addition of saturated $NaHCO_3$ and extracted with ether (3 x 50 ml). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and evaporated in vacuo. Column chromatography on silica gel (5% hexane-ethyl acetate) gave **7a** (0.22 g, 86%) as a white solid, mp 156-158°C (CH_2Cl_2) (lit.,[17] 156-157°C). Compound (**7a**) was also obtained by the same method from **5b**; the yield was 85%. Compound (**7b-f**) and (**8a**) were similarly obtained.

4-Methyl-2-azafluorenone (**7b**)

Yield 95% from **5c**; White solid; mp 131-132°C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$) δ 8.69 (1H, s, pyridyl H-2), 8.50 (1H, s, pyridyl H-6), 7.71 (2H, dd, J = 0.8, 7.7 Hz, aryl 2H), 7.58-7.44 (2H, m, aryl 2H), 2.60 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 2996, 2973, 1710 (C=O), 1595, 1443, 1301, 1201, 1130; ms m/z: 195 (M^+, 100), 167 (25), 139 (23); Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.80; H, 4.36; N, 7.08.

3-Methyl-2-azafluorenone (**7c**)

Yield 81% from **5d**; Pale yellow solid; mp 138-140°C (CH_2Cl_2) ; ^{1}H-nmr ($CDCl_3$) δ 8.74 (1H, s, pyridyl H-2), 7.74 (1H, dd, J = 0.9, 7.3 Hz, aryl H), 7.63-7.41 (3H, m, aryl 3H), 7.34 (1H, s, pyridyl H-5), 2.64 (3H, s, methyl); ir (cm^{-1}) ($CHCl_3$): 2971, 1714 (C=O), 1610, 1447; ms m/z: 195 (M^+, 100), 181 (7), 166 (7), 139

(14); Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.74; H, 4.25; N, 7.12.

7-Methyl-2-azafluorenone (**7d**)

Yield 89% from **5e**; Yellow solid; mp 130-132°C (CH_2Cl_2) (lit.,[2] 120-122°C).

7-Fluoro-2-azafluorenone (**7e**)

Yield 53% from **5f** or yield 40% from **5g**; Yellow solid; mp 173-175°C (CH_2Cl_2); ^{1}H-nmr ($CDCl_3$) δ 8.86 (1H, s, pyridyl H-2), 8.76 (1H, d, J = 4.5 Hz, pyridyl H-6), 7.64 (1H, q, J = 2.4 Hz, aryl H), 7.46 (2H, m, aryl 2H), 7.31 (1H, m, pyridyl H-5); ir (cm^{-1}) ($CHCl_3$): 2988, 1723 (C=O), 1596, 1459, 1267; ms m/z: 199 (M^+, 100), 171 (29), 144 (38); Anal. Calcd for $C_{12}H_6NOF$: C, 72.36; H, 3.04; N, 7.04. Found: C, 72.55; H, 3.23; N, 6.76.

7-Chloro-2-azafluorenone (**7f**)

Yield 48% from **5h**; Yellow solid; mp 152-153°C (CH_2Cl_2/hexane) (lit.,[2] 150-152°C).

5*H*[1]Benzopyrano[3,4-*c*]pyridin-5-one (**8a**)

Yield 78% from **5i**; White solid; mp 164-166°C (CH_2Cl_2) (lit.,[7] 162-164°C).

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