Table I. Experimental Data for Picrates

picrate of	yield, %	mp, °C	recryst solvent
2-amino-3-bromo-5-methylpyridine (*1*)[a]	94	261	acetone
3-amino-2-chloropyridine (*1*)	82	168	ethanol
2-amino-5-bromo-3-methylpyridine (*2*)	95	259	acetone
2-amino-3-methyl-5-nitropyridine (*3*)	86	252	acetone
2-amino-5-methyl-3-nitropyridine (*3*)	89	244	acetone
3-amino-2-chloro-5-methylpyridine (*4*)	74	160	ethanol
5-amino-2-chloro-3-methylpyridine (*5*)	88	172	ethanol
3-amino-2-bromo-5-methylpyridine (*6*)	51	151	ethanol–water
5-amino-2-bromo-3-methylpyridine (*6*)	85	176	ethanol

[a] Numbers in parentheses are literature references for the preparation of the aminopyridines.

mL) with magnetic stirring and slight warming. (In the case of the nitropyridines a mixture of 40 mL of ethanol and 40 mL of acetone was required.) Picric acid (1.15 g, 0.005 mol) was added in one portion to the stirred amine solution and the resulting mixture was slowly warmed to 50 °C for 10 min with continued stirring. The yellow suspension was cooled to 10 °C, and the crude picrate was collected by filtration and washed with cold ethanol. Recrystallization was performed as indicated in Table I.

Registry No. 2-Amino-3-bromo-5-methylpyridine picrate, 98875-88-8; 3-amino-2-chloropyridine picrate, 98875-89-9; 2-amino-5-bromo-3-methylpyridine picrate, 98875-90-2; 2-amino-3-methyl-5-nitropyridine picrate, 98875-91-3; 2-amino-5-methyl-3-nitropyridine picrate, 98875-92-4; 3-amino-2-chloro-5-methylpyridine picrate, 98875-93-5; 5-amino-2-chloro-3-methylpyridine picrate, 98875-94-6; 3-amino-2-bromo-5-methylpyridine picrate, 98875-95-7; 5-amino-2-bromo-3-methylpyridine picrate, 98875-96-8.

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A Convenient Synthesis of Fluorinated 2,4,6-Triarylpyridines via 4-Picolinium Ylides

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The reaction of 2-naphthoyl-4-picolinium methylide with fluoro-substituted benzylideneacetophenones gave a variety of fluorinated 2,4,6-triarylpyridines. The structural assignment of the pyridines was made on the basis of elemental analysis and spectroscopic evidence and the use of a known synthetic route and procedures.

Experimental Section

The structure of compounds **5** was established by microanalyses and physical and spectral data (Table I). Melting points were measured on a Gallen-Kamp apparatus and are uncorrected. The NMR spectra ($CDCl_3$) were recorded on a Varian A-60 and A-90 spectrophotometer with tetramethylsilane as the internal standard. IR spectra (KBr) are recorded on a Perkin-Elmer infracord spectrophotometer. Analytical samples were purified by column chromatography over silica gel. Purity was checked by thin layer chromatography.

The IR spectrum of the products in general exhibited the aromatic absorption bands in the region 3000–3030 cm^{-1}. The strong bands in the region 1500–1600 cm^{-1} have been assigned to the interaction between C=C and C=N vibrations to the pyridine ring. The bands due to ring vibrations and C–H deformations are observed near 1245 and 1020 cm^{-1}.

2-Naphthoyl-4-picolinium methyl bromide was prepared by treatment of 2-naphthoylmethyl bromide and 4-picoline in benzene at reflux temperature according to the Krohnke (*1*) method.

Preparation of Fluorinated 2,4,6-Triarylpyridines. A general procedure (*2*) was used in all the reactions (Scheme I).

Scheme I

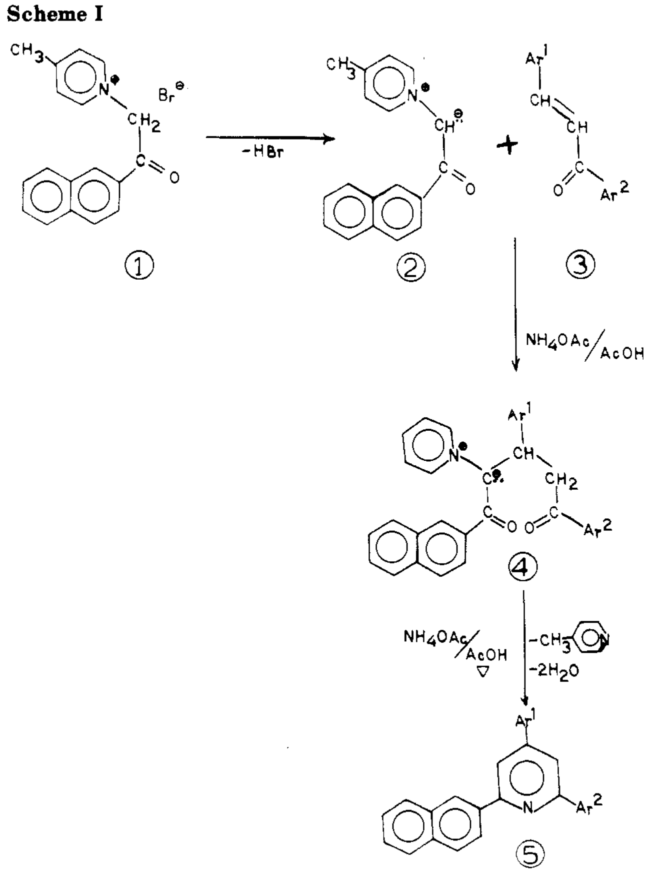

Table I. Structure, Physical Properties, and NMR Data of Fluoro-Substituted 2,4,6-Triarylpyridines (5)[a]

compd	Ar^1	Ar^2	yield, %	mp, °C	crystllg solvent	NMR data: ^1H NMR ($CDCl_3$) δ, ppm	no. of protons	assignt
5a	$4\text{-F}\cdot C_6H_4$	C_6H_5	62	128–30	py/H_2O	7.00–8.70 m	18 H	aromatic
5b	$4\text{-F}\cdot C_6H_4$	$4\text{-Cl}\cdot C_6H_4$	68	175–78	py/H_2O			
5c	$4\text{-F}\cdot C_6H_4$	$4\text{-Br}\cdot C_6H_4$	55	180–82	py/MeOH			
5d	$4\text{-OCH}_3\cdot C_6H_4$	$4\text{-F}\cdot C_6H_4$	56	140–44	py	7.00–8.80 m	17 H	aromatic
						3.92 S	3 H	methoxy
5e	$4\text{-F}\cdot C_6H_4$	2-naphthyl	63	175–6	py	6.80–8.60 m	23 H	aromatic
5f	$3,4\text{-(OCH}_3)_2\cdot C_6H_3$	$4\text{-F}\cdot C_6H_4$	59	175–8	py/MeOH	7.80–8.90 m	16 H	aromatic
						4.03 S	3 H	methoxy
						4.07 S	3 H	methoxy
5g	$4\text{-F}\cdot C_6H_4$	$4\text{-F}\cdot C_6H_4$	50	168–70	py	6.78–8.60 m	17 H	aromatic
5h	$4\text{-N(CH}_3)_2\text{–}C_6H_4$	$4\text{-F}\cdot C_6H_4$	35	190–92	py	6.89–8.60 m	17 H	aromatic
						1.52 S	6 H	*N*-dimethyl
5i	$4\text{-NO}_2\cdot C_6H_4$	$4\text{-F}\cdot C_6H_4$	39	192–96	py/H_2O			
5j	$4\text{-F}\cdot C_6H_4$	$4\text{-OCH}_3C_6H_4$	40	152–4	py	7.00–8.88 m	17 H	aromatic
						3.92 S	3 H	methoxy
5k	$4\text{-F}\cdot C_6H_4$	$4\text{-CH}_3C_6H_4$	52	124–6	$CHCl_3$/MeOH	7.00–8.90 m	17 H	aromatic
						2.50 S	3 H	methyl

[a] All the compounds gave satisfactory elemental analysis.

To a stirred solution of 3 mmol of picolinium salt in 10 mL of acetic acid in the presene of ammonium acetate was added gradually a solution of fluoro-substituted chalcone (3 mmol) in 10 mL of glacial acetic acid under an inert atmosphere of nitrogen. The reaction mixture was stirred at reflux temperature for 6 h, and was kept at room temperature overnight. The mixture was finally poured into ice-cold water (20 mL). The precipitated solid product was isolated by suction, washed with water and methanol, dried, and recrystallized from a suitable solvent.

The nature of the solvent used in place of acetic acid has a pronounced influence on the reaction rate. In dimethylformamide the reaction proceeds much slower than in acetic acid and in dimethyl sulfoxide no reaction is observed.

Registry No. 1, 6277-78-7; **3a**, 1608-51-1; **3b**, 98991-31-2; **3c**, 98991-32-3; **3d**, 2965-64-2; **3e**, 398-46-9; **3f**, 28081-14-3; **3g**, 2805-56-3; **3h**, 28081-19-8; **3i**, 2805-54-1; **3j**, 2965-63-1; **3k**, 98991-33-4; **5a**, 98991-34-5; **5b**, 98991-35-6; **5c**, 98991-36-7; **5d**, 98991-37-8; **5e**, 98991-38-9; **5f**, 98991-39-0; **5g**, 98991-40-3; **5h**, 98991-41-4; **5i**, 98991-42-5; **5j**, 98991-43-6; **5k**, 98991-44-7.

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