Table III. ^{13}C NMR Data

compd	chemical shifts[a] ($CDCl_3/Me_4Si_{int}$), ppm
5a	29.1 (C-1); 20.6 (C-2); 21.9[b] (C-3); 28.4 (C-4); 121.6 (C-5); 133.1 (C-6); 129.2 (C-7); 126.4 (C-8); 156.8 (C-9); 136.4_5 (C-11); 128.3 (C-12); 135.7_5 (C-13); 155.2 (C-14)
5c	29.1 (C-1); 20.7[c] (C-2); 22.0[c] (C-3); 28.6 (C-4); 122.2 (C-5); 133.2 (C-6); 129.2 (C-7); 126.5_5 (C-8); 155.7 (C-9); 136.3 (C-11); 129.1 (C-12); 136.8 (C-13); 155.4 (C-14); 37.5 (CH_2-1′); 30.4 (CH_2-2′); 29.0_5[d] (CH_2-3′); 29.0[d] (CH_2-4′); 28.6[d] (CH_2-5′); 31.7 (CH_2-6′); 22.6 (CH_2-7′); 14.0 (CH_3)
5d	29.1_5 (C-1); 20.8[e] (C-2); 22.1[e] (C-3); 28.7 (C-4); 122.1 (C-5); 133.2 (C-6); 129.2 (C-7); 126.6 (C-8); 155.7 (C-9); 136.4 (C-11); 129.2 (C-12); 136.8 (C-13); 155.4 (C-14); 37.5 (CH_2-1′); 30.4 (CH_2-2′); 28.6[f] (CH_2-3′); 28.6[f] (CH_2-4′); 29.4[f] (CH_2-5′); 29.0[f] (CH_2-6′); 29.1_5[f] (CH_2-7′); 31.9 (CH_2-8′); 22.6_5 (CH_2-9′); 14.0_5 (CH_3)
5e	29.1 (C-1); 20.4_5[g] (C-2); 21.7[g] (C-3); 28.4 (C-4); 121.7 (C-5); 133.1 (C-6); 129.5 (C-7); 126.6 (C-8); 155.7 (C-9); 136.5 (C-11); 129.3 (C-12); 137.9 (C-13); 155.7 (C-14); 41.4 (CH_2-1′); 136.2 (C_{arom}1″); 128.5 (C_{arom}2″); 128.5 (C_{arom}3″); 127.9 (C_{arom}4″)
5j	28.9 (C-1); 20.0_5[h] (C-2); 21.3[h] (C-3); 28.1 (C-4); 120.9 (C-5); 132.8 (C-6); 12..1 (C-7); 126.5_5 (C-8); 151.9 (C-9); 136.3 (C-11); 128.3 (C-12); 137.1 (C-13); 156.3 (C-14); 33.2_5 (CH_2-1′); 24.5 (CH_2-2′); 55.0 (CH_2-3′); 41.9 (CH_3)
5k	29.1 (C-1); 20.2[i] (C-2); 21.4[i] (C-3); 28.2 (C-4); 121.6 (C-5); 132.7 (C-6); 129.1 (C-7); 126.4 (C-8); 149.2 (C-9); 137.2 (C-11); 128.7 (C-12); 137.7 (C-13); 156.8 (C-14); 29.4 (CH_2-1′); 55.3 (CH_2-2′); 41.8 (CH_3)
6a	29.4_5 (C-1); 20.7[j] (C-2); 22.0[j] (C-3); 28.7 (C-4); 122.6 (C-5); 133.0 (C-6); 129.3 (C-7); 126.1 (C-8); 153.0 (C-9); 136.7 (C-11); 129.0 (C-12); 137.4 (C-13); 156.1 (C-14); 35.3_5 (CH_2-α,α'); 30.9 (CH_2-β,β')
6b	29.2 (C-1); 20.7[k] (C-2); 22.0[k] (C-3); 28.7 (C-4); 122.4 (C-5); 133.3 (C-6); 129.4 (C-7); 126.2 (C-8); 154.0 (C-9); 136.6 (C-11); 129.0 (C-12); 1368 (C-13); 155.7_5 (C-14); 36.4 (CH_2-α,α'); 2995 (CH_2-β,β')
6c	29.2_5 (C-1); 20.7[l] (C-2); 22.0[l] (C-3); 28.7 (C-4); 122.2 (C-5); 133.3 (C-6); 129.3 (C-7); 126.4 (C-8); 155.0 (C-9); 136.5 (C-11); 129.0_5 (C-12); 136.8 (C-13); 155.6 (C-14); 37.0 (CH_2-α,α'); 29.9 (CH_2-β,β'); 27.7_5 (CH_2-γ,γ')
6d	29.1 (C-1); 20.7[m] (C-2); 22.0[m] (C-3); 28.7 (C-4); 122.1_5 (C-5); 133.3 (C-6); 129.3 (C-7); 126.5 (C-8); 155.3 (C-9); 136.4 (C-11); 129.1 (C-12); 136.8 (C-13); 155.5 (C-14); 37.1_5 (CH_2-α,α'); 30.2_5 (CH_2-β,β'); 28.2 (CH_2-γ,γ')

[a] Recorded with a Bruker AM 200 spectrometer. [b-m] These attributions may be commuted.

Hydrochloride is precipitated by addition of ether in a wide quantity. The salt is recrystallized from either an ethanol–ether mixture or an ethanol–acetone mixture.

Acknowledgment

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Registry No. **2**, 82791-68-2; **3a**, 99053-30-2; **3e**, 99053-52-8; **3f**, 99053-53-9; **3g**, 99053-54-0; **3h**, 99053-55-1; **4b**, 99053-56-2; **4c**, 99053-57-3; **4d**, 99053-58-4; **5a**, 99053-31-3; **5b**, 99053-32-4; **5c**, 99053-33-5; **5d**, 99053-34-6; **5e**, 99053-35-7; **5f**, 99053-36-8; **5g**, 99053-37-9; **5h**, 99053-38-0; **5i**, 99053-39-1; **5j**, 99053-40-4; **5k**, 99053-41-5; **5l**, 99053-42-6; **5m**, 99053-43-7; **6a**, 99053-44-8; **6b**, 99053-45-9; **6c**, 99053-46-0; **6d**, 99053-47-1; **6e**, 99053-48-2; **6f**, 99053-49-3; **6g**, 99053-50-6; **6h**, 99053-51-7; CH_3Br, 74-83-9; $C_5H_{11}Br$, 110-53-2; $C_8H_{17}Br$, 111-83-1; $C_{10}H_{21}Br$, 112-29-8; $BrCH_2C_6H_5$, 100-39-0; 2-$BrCH_2C_6H_4Cl$, 611-17-6; 3-$BrCH_2C_6H_4Cl$, 766-80-3; 4-$BrCH_2C_6H_4Cl$, 622-95-7; 3-$BrCH_2C_6H_4CF_3$, 402-23-3; $Br(CH_2)_2N(CH_3)_2$, 5459-68-7; $Br(CH_2)_3N(CH_3)_2$, 53929-74-1; $Br(CH_2)_2N(CH_2CH_3)_2$, 5392-81-4; $Br(CH_2)_2N(CH(CH_3)_2)_2$, 90221-88-8; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5.

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Picrates of Some Ring-Substituted 2-Amino- and 3-Aminopyridines

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The preparation of the picrates of nine ring-substituted 2-amino- and 3-aminopyridines is described. Melting points and methods of purification are also presented.

In past years we have prepared various ring-substituted 2-amino- and 3-aminopyridines as synthetic intermediates. Since picrates are one of the better qualitative analytical derivatives for amines, and since the picrate derivatives for the aforementioned aminopyridines have never been reported, we now wish to report the preparation and melting points of these picrates.

Elemental analyses (C, H, N) in agreement with theoretical values, and which confirm 1:1 stoichiometry for the picrate salts, were obtained and submitted for review. Experimental data for the picrates are reported in Table I.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

Picrate Formation—General Procedure. The appropriate aminopyridine (0.005 mol) was dissolved in absolute ethanol (35

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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

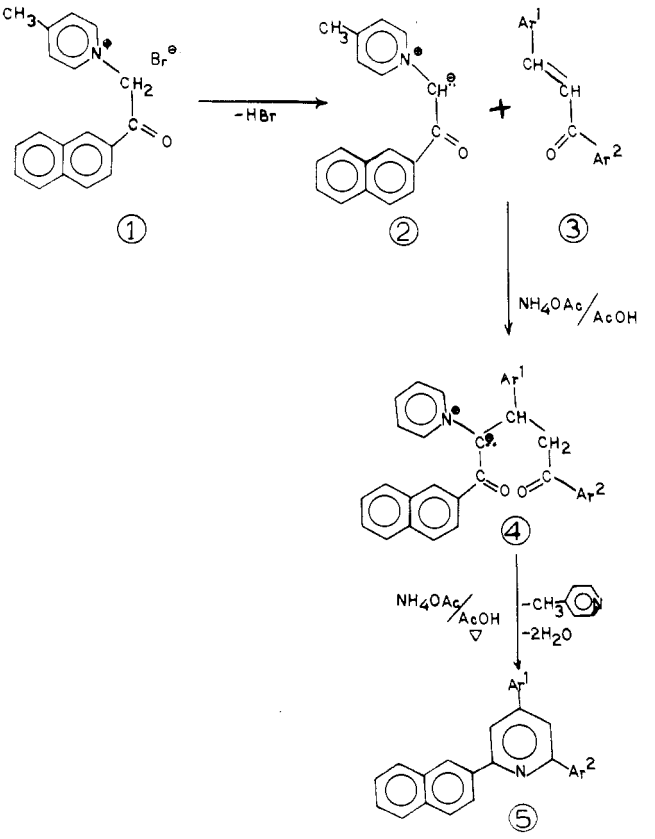
The structure of compounds **5** was established by microanalyses and physical and spectral data (Table I). Melting points were measured on a Gallen-Kamp apparatus and are uncorrected. The NMR spectra ($CDCl_3$) were recorded on a Varian A-60 and A-90 spectrophotometer with tetramethylsilane as the internal 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



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