Synthesis of 4-hydroxy- and 3-acyl-4-amino-2-trifluoromethylpyridines

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Schemes for synthesizing 3-acyl-4-amino(hydroxy)-2-trifluoromethylpyridines from 3-acyl-4-amino-5,5,5-trifluoro-3-penten-2-ones *via* their diphenylboron chelate complexes have been suggested.

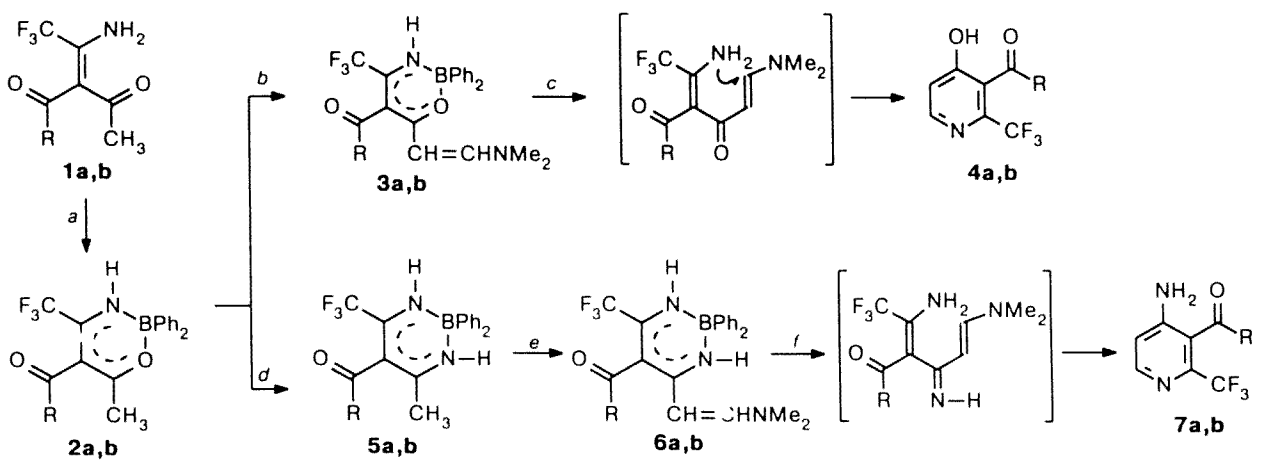
Key words: diphenylboron chelates, 3-acetyl(benzoyl)-4-amino-5,5,5-trifluoro-3-penten-2-one, β-diiminates, dimethylformamide dimethylacetal, 3-acyl-4-amino(hydroxy)-2-trifluoromethylpyridines, chelate organic synthesis.

Heterocyclic compounds containing a CF_3 group possess a wide spectrum of biological activity.[1,2] Recently, we suggested[3] a simple scheme for synthesizing 4-hydroxy-2-trifluoromethylpyridine (HTP) involving the preparation of the diphenylboron chelate of 4-amino-5,5,5-trifluoro-3-penten-2-one,[4] the reaction of this complex with DMF dimethylacetal (DMF DMA), and cyclization of the condensation product in boiling BuOH. An analogous approach has been employed for synthesizing 3-ethoxycarbonyl-HTP from ethyl 3-amino-2-acetyl-4,4,4-trifluoro-2-butenoate.[5]

In a continuation of these studies based on the use of the "methodology of chelate organic syntheses" we have developed methods for obtaining previously unknown 3-acyl-HTP and 3-acyl-4-amino-2-trifluoromethylpyridines from 3-acyl-4-amino-5,5,5-trifluoro-3-penten-2-ones **(1a,b)**, which are easily synthesized from the corresponding β-diketones and trifluoroacetonitrile in the presence of catalytic amounts of $Ni(acac)_2$.[6] Recently, it has been shown (see Ref. 7) that enaminone **1a** is smoothly borylated by Ph_2BOBu to form the diphenylboron chelate **2a**. Analogously, complex **2b** has been obtained from enaminone **1b** in 86% yield (Scheme 1).

The borylation of compounds **1a,b** proceeds regiospecifically. The data of the IR and NMR spectra of chelates **2a,b** substantiate that the NH_2 and MeCO groups of the original ligands are involved in the coordination interaction with the boron atom. In particular, the signal of MeCO in the ^{13}C NMR spectrum of chelate **2b** occurs in a substantially stronger field (δ 188.29 ppm) than that for enaminone **1b** (δ 197.06 ppm),

Scheme 1



R = Me (**a**); Ph (**b**)

Reagents and conditions: *a*) Ph_2BOBu, CH_2Cl_2, –20 °C, 20 h; *b*) DMF DMA (ether, –20 °C, 1 h for **3a**; benzene, Δ, 3 h for **3b**); *c*) BuOH, Δ, 3—6 h; *d*) NH_3, toluene, 120—140 °C, (sealed tube); *e*) DMF DMA (benzene, Δ, 6 h for **6a**; toluene, Δ, 15 h for **6b**); *f*) BuOH, Δ, 8—15 h.

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whereas the difference in the chemical shifts of PhCO for the complex and the free ligand is not large. This indicates that in coordination interactions the benzoyl group of enaminone **1b** remains free (refer to the known data[4,8] on variations in chemical shifts (CS) of the C atom in the carbonyl group of functionalized enaminones as they form B-chelates).

Chelates **3a,b**, whose structure has been proved by spectroscopic data (IR, ^1H and ^{13}C NMR, and mass spectra), were obtained by the condensation of complexes **2a,b** with DMF DMA. These transformations are analogous to the reaction of DMF DMA with the diphenylboron chelate of deacetylated **1a** (*cf.* Ref. 4).

The decomposition of complexes **3a,b** in boiling BuOH is accompanied by cyclization of the free ligands evolved into 3-acyl-HTP (**4a,b**) with elimination of Me_2NH. Crystalline compounds **4a,b** are readily soluble in alcohol, ether, and acetone, somewhat less soluble in benzene and $CHCl_3$, and are insoluble in hexane and water.

The IR spectroscopic data of compounds **4a,b** in KBr and in solvents testify that the hydroxypyridine $\rightleftharpoons$ pyridone equilibrium is shifted substantially towards the hydroxy-form. Thus, **4a** in the solid state and in DMSO exhibits only the band at 1710 cm^{-1} in the absorption region of carbonyl groups (ν(C=O) of the acetyl group). A significant decrease in the absorption intensity in the 1710—1720 cm^{-1} region and the appearance of a band at ~1660 cm^{-1} is typical of the spectra of diluted solutions of **4a** in nonpolar solvents. This can be accounted for by the participation of the acetyl group in the formation of an intramolecular hydrogen bond O—H...O=C (intermolecular O—H...N interaction is more typical of concentrated solutions).

The ^{13}C NMR spectroscopic data for **4a,b** in DMSO-d_6 corroborate that these compounds exist almost entirely in the form of hydroxypyridines. Thus, the CS of the C(4) atoms (162.68 ppm for **4a** and 162.88 ppm for **4b**) are comparable to the CS of the corresponding atom in 4-methoxypyridine[9] (164.9 ppm).

It has been found recently[7] that a distinctive property of chelate **2a** is its ability to replace the endocyclic O-atom with an N-alkylated fragment under the action of primary aliphatic amines. Similarly, complexes have been synthesized in the present study from compounds **2a,b** and NH_3 (heating in toluene in a sealed tube) which, according to the IR, ^1H and ^{13}C NMR, and mass spectra, have the structure of β-diiminate-type chelates **5a,b**.

The presence of a free acyl group in molecules **5a,b** is confirmed, in particular, by the ^{13}C NMR spectra (for instance, the CS of the carbonyl C atom in the spectrum of **5a** in $CDCl_3$ is 197.84 ppm).

Chelates **5a,b** are stable in air and readily soluble in DMSO, acetone, and $CHCl_3$.

When heated with DMF DMA they afford condensation products **6a,b**, which have a chelate structure and were further used without purification (compound **6a** was explicitly isolated and identified in an analytically pure form). When boiled in butanol, chelates **6a,b** afford 3-acyl-4-amino-2-trifluoromethylpyridines (**7a,b**) (similarly to the formation of 4-hydroxypyridines **4a,b** from complexes **3a,b**).

Crystalline compounds **7a,b** are readily soluble in alcohol, ether, and acetone, and are insoluble in hexane and water. Their IR spectra in $CHCl_3$ exhibit absorption characteristic of νNH_2 (two bands at 3500 and 3400 cm^{-1}) and ν(C=O) (1705 cm^{-1} for **7a** and 1665 cm^{-1} for **7b**). The data of ^1H, ^{13}C NMR, and mass spectra are also consistent with structures **7a,b**.

It has been previously noted in a preliminary communication[7] that *N*-alkylated derivatives of **5a** react with two equivalents of DMF DMA (both methyl groups of the complex are involved in the condensation), which ultimately allows the synthesis of substituted 1,6-naphthyridine-(1*H*)-4-ones. However, the interaction of **5a** itself with excess DMF DMA proceeds in a more complicated way, and attempts to isolate the corresponding naphthyridinone after treating the condensation products with boiling butanol failed, while the yield of **7a** drastically decreased.

Azines containing vicinal NH_2 and Ac (Bz) groups are convenient building blocks for fused nitrogen-containing heterocycles.[10—12] Therefore, compounds **7a,b** can be regarded as potential reagents for synthesizing bicyclic systems with a trifluoromethyl group.

Experimental

^1H and ^{13}C NMR spectra were registered on Bruker WM-250 (250.13 MHz) and Bruker AM-300 (75.45 MHz) spectrometers, respectively, with reference to TMS. IR spectra were recorded on UR-20 or Perkin-Elmer 577 instruments. Mass spectra were obtained on a Varian MAT-311A instrument.

Diphenylboron chelate of 3-acetyl-4-amino-5,5,5-trifluoro-3-penten-2-one (2a) was synthesized using a reported procedure.[7]

4-Amino-3-benzoyl-5,5,5-trifluoro-3-penten-2-one (1b) was obtained from benzoylacetone and CF_3CN in the presence of catalytic amounts of $Ni(acac)_2$, analogously[6] to **1a**. Benzoylacetone (10.0 g, 61.6 mmol) and 0.16 g of $Ni(acac)_2$ in 20 ml of dry CH_2Cl_2 were placed in a two-necked flask with a "cold finger"-type reflux condensor (filled with solid CO_2 and acetone). Then 8.78 g (92.4 mmol) of CF_3CN were slowly passed in over a period of 8 h, and the mixture was left for 12 h. The solvent was distilled off under reduced pressure, and 50 ml of hexane were added to the residue. The precipitate was filtered off and sublimated *in vacuo* (120—150 °C, 1—2 Torr). Enaminone **1b** (14.34 g) contaminated by a small amount of benzoylacetone was obtained. Analytically pure **1b** was obtained by purification on a column with SiO_2 (CCl_4 as the eluent). The isolated yield was 10.0 g (64%) of **1b**, m.p. 109—110 °C. Found (%): C, 56.52; H, 3.96; N, 5.58. $C_{12}H_{10}F_3NO_2$. Calculated (%): C, 56.03; H, 3.89; N, 5.45. IR ($CHCl_3$, ν/cm^{-1}): 3470 (NH); 3230—3160 (NH); 1665 (C=O); 1640, 1600. ^1H NMR (DMSO-d_6, δ, ppm): 1.84 (s, 3 H, Me); 7.50—7.90 (m, 5 H, Ph); 9.50 (br.s, 2 H, NH_2). ^{13}C NMR ($CDCl_3$, δ, ppm, *J*/Hz): 29.41 (q, MeCO, ^1J = 128); 108.96 (s, AcC); 120.02 (q, CF_3, $^1J_{C,F}$ = 279); 128.80; 129.51; 133.80;

138.22 (Ph); 147.10 (q, CN, $^2J_{C,F}$ = 34); 194.90 (s, PhCO); 197.06 (q, MeCO, ^2J = 5.6).

Diphenylboron chelate of 4-amino-3-benzoyl-5,5,5-trifluoro-3-penten-2-one (2b). A mixture of 3.0 g (11.7 mmol) of **1b** and 3.5 g (14.7 mmol) of Ph_2BOBu in 15 ml of CH_2Cl_2 was left for 20 h at ~20 °C (TLC was used to follow the course of the reaction). The solvent was distilled off under reduced pressure and 15 ml of hexane were added to the residue. The precipitate was filtered off and washed with pentane to obtain 4.2 g (86%) of chelate **2b**, m.p. 153—154 °C. Found (%): C, 68.37; H, 4.67; N, 3.40. $C_{24}H_{19}BF_3NO_2$. Calculated (%): C, 68.40; H, 4.51; N, 3.32. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.27 (s, 3 H, Me); 7.22—7.57 (m, 15 H, 3 Ph); 7.60 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$, δ, ppm, *J*/Hz): 23.64 (q, Me, ^1J = 129); 109.46 (s, $CF_3\underline{C}\underline{C}$); 118.70 (q, CF_3, $^1J_{C,F}$ = 281); 127.28; 127.67; 128.78; 129.54; 131.97; 133.84; 138.48; 146.0 (3 Ph); 155.70 (q, CN, $^2J_{C,F}$ = 36); 188.29 (q, Me$\underline{C}$O, ^2J = 6.0); 191.40 (Ph$\underline{C}$O).

Diphenylboron chelate of 4-acetyl-5-amino-6,6,6-trifluoro-1-dimethylamino-1,4-hexadien-3-one (3a). DMF DMA (0.8 g, 6.8 mmol) was added to a solution of 1.0 g (2.8 mmol) of **2a** in 10 ml of ether and the mixture was left for 1 h at ~20 °C. The volatile products were evaporated off under reduced pressure, and the residue was purified on a column with SiO_2 (eluent: benzene—hexane, 1 : 1). Chelate **3a** (1.1 g, 97%) was isolated, m.p. 158—159 °C (benzene—hexane). Found (%): C, 64.05; H, 5.45; F, 14.11; N, 6.66. $C_{22}H_{22}BF_3N_2O_2$. Calculated (%): C, 63.70; H, 5.35, F, 13.76; N, 6.76. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 2.26 (s, 3 H, MeCO); 2.97 (s, 3 H, MeN) and 3.24 (s, 3 H, MeN); 5.62 (d, 1 H, $\underline{C}\underline{H}$, *J* = 12); 6.62 (br.s, 1 H, NH); 7.22—7.55 (m, 10 H, 2 Ph); 8.05 (d, 1 H, CHN, *J* = 12). ^{13}C NMR ($CDCl_3$, δ, ppm, *J*/Hz): 33.05 (q, $\underline{Me}$CO, ^1J = 129); 37.82 (q, MeN, ^1J = 139) and 46.01 (q, MeN, ^1J = 142); 90.91 (d, $\underline{C}\underline{H}$=CN, ^1J = 161); 108.00 (s, $CF_3\underline{C}\underline{C}$); 120.02 (q, CF_3, $^1J_{C,F}$ = 278); 126.38; 127.28; 132.03; 151.15 (2 Ph); 152.10 (q, $CF_3\underline{C}$N, $^2J_{C,F}$ = 34); 156.20 (d, CHN, ^1J = 169); 176.32 (s, COB); 199.28 (q, Me$\underline{C}$O, ^2J = 7.0).

Diphenylboron chelate of 5-amino-4-benzoyl-6,6,6-trifluoro-1-dimethylamino-1,4-hexadien-3-one (3b). A mixture of 1.0 g (2.37 mmol) of **2b** and 0.31 g (2.60 mmol) of DMF DMA in 10 ml of benzene was refluxed for 3 h, and the solvent was evaporated under reduced pressure. Hexane (10 ml) was added to the residue, and the crystals were filtered off and washed with hexane to obtain 1.05 g (92%) of chelate **3b**, m.p. 148—149 °C. Found (%): C, 68.12; H, 5.30; N, 5.99. $C_{27}H_{24}BF_3N_2O_2$. Calculated (%): C, 68.06, H, 5.04, N, 5.88. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 2.78 (s, 3 H, MeN) and 3.20 (s, 3 H, MeN); 5.30 (d, 1 H, CH, *J* = 12); 6.68 (br.s, 1 H, NH); 7.11—7.55 (m, 15 H, 3 Ph); 8.02 (d, 1 H, NCH, *J* = 12).

3-Acetyl-2-trifluoromethyl-4-hydroxypyridine (4a). A mixture of 1.0 g (2.40 mmol) of chelate **3a** and 10 ml of BuOH was refluxed for 3 h; the excess BuOH was evaporated off under reduced pressure, and the residue was chromatographed on a column with SiO_2 (eluents: $CHCl_3$ first and then, $CHCl_3$—acetone, 8 : 1 and 5 : 1) to get 0.4 g (81%) of pyridine **4a**, which was purified by sublimation *in vacuo* (90 °C, 1—2 Torr), m.p. 141—142 °C (benzene). Found (%): C, 46.60; H, 2.56; N, 6.82. $C_8H_6F_3NO_2$. Calculated (%): C, 46.84; H, 2.95; N, 6.83. Mass spectrum, *m/z*: 205 $[M]^+$. ^{1}H NMR (DMSO-d_6, δ, ppm, *J*/Hz): 2.49 (s, 3 H, Me); 7.14 (d, 1 H, CH(5), *J* = 5.0); 8.43 (d, CH(6), *J* = 5.3); 12.0 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6, δ, ppm, *J*/Hz): 31.56 (q, Me, ^1J = 129); 114.73 (d, C-5, ^1J = 171); 121.55 (q, CF_3, $^1J_{C,F}$ = 276); 125.87 (s, C-3); 142.64 (q, C-2, $^2J_{C,F}$ = 34); 150.71 (d, C-6, ^1J = 183); 162.68 (d, C-4, ^2J = 7.0); 200.6 (q, CO, ^2J = 7.0).

3-Benzoyl-2-trifluoromethyl-4-hydroxypyridine (4b). Chelate **3b** (1.0 g, 2.10 mmol) was refluxed with 10 ml of BuOH for 6 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a column with SiO_2 (eluent: benzene — acetone, 5 : 1) to isolate 0.45 g (81%) of pyridine **4b**, m.p. 189—190 °C. Found (%): C, 58.38; H, 3.13; N, 5.27. $C_{13}H_8F_3NO_2$. Calculated (%): C, 58.42; H, 2.99; N, 5.24. Mass spectrum, *m/z*: 267 $[M]^+$. IR ($CHCl_3$, ν/cm^{-1}): 3550 (OH); 1675 (CO). ^{1}H NMR (DMSO-d_6, δ, ppm, *J*/Hz): 7.22 (d, 1 H, CH(5), *J* = 5.5); 7.40—7.85 (m, 5 H, Ph); 8.55 (d, 1 H, CH(6), *J* = 5.5); 12.0 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6, δ, ppm, *J*/Hz): 114.26 (d, C-5, ^1J = 165); 121.20 (q, CF_3, $^1J_{C,F}$ = 278); 123.01 (s, C-3); 128.60; 128.78; 133.87; 136.17 (Ph); 143.42 (q, C-2, $^2J_{C,F}$ = 32); 150.89 (d, C-6, ^1J = 184); 162.88 (d, C-4, ^2J = 7.0); 192.27 (CO).

Diphenylboron chelate of 4-amino-3-trifluoroacetimidoyl-3-penten-2-one (5a). A mixture of 0.5 g (1.4 mmol) of **2a** and 22 ml (2.8 mmol) of a 0.13 *M* NH_3 solution in absolute toluene was heated for 15 h at 120—140°C in a sealed tube. The solvent was then distilled off under reduced pressure, and the residue was chromatographed on a column with SiO_2 (eluent: benzene — acetone, 5 : 1) to isolate 0.3 g (60%) of chelate **5a**, m.p. 184—185 °C. Found (%): C, 63.68; H, 5.06; N, 7.81. $C_{19}H_{18}BF_3N_2O$. Calculated (%): C, 64.41; H, 5.34; N, 7.91. IR ($CHCl_3$, ν/cm^{-1}): 3390 (NH); 3370 (NH); 1675 (CO). Mass spectrum, *m/z*: 281 $[M-Ph]^+$. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.29 (s, 3 H, Me); 2.36 (s, 3 H, Me); 6.52 (br.s, 1 H, NH); 6.88 (br.s, 1 H, NH); 7.18—7.48 (m, 10 H, 2 Ph). ^{13}C NMR ($CDCl_3$, δ, ppm, *J*/Hz): 24.74 (q, Me, ^1J = 129); 32.53 (q, MeCO, ^1J = 129); 105.98 (s, $CF_3\underline{C}\underline{C}$); 119.95 (q, CF_3, $^1J_{C,F}$ = 280); 126.77; 127.62; 132.26; 150 (2Ph); 151.03 (q, $CF_3\underline{C}$N, $^2J_{C,F}$ = 34); 167.55 (s, CN); 197.84 (q, CO, ^2J = 6.0).

Diphenylboron chelate of 3-amino-2-trifluoroacetimidoyl-1-phenyl-2-buten-1-one (5b). A mixture of 2.5 g (5.94 mmol) of **2b** and 40 ml (12 mmol) of a 0.3 *M* NH_3 solution in absolute toluene was heated in a sealed tube at 120—140 °C for 15 h. The solvent was distilled off under reduced pressure, and the residue was recrystallized from 10 ml of a toluene : hexane mixture, 1 : 5, followed by purification on a column with SiO_2 (eluent: benzene — acetone, 10 : 1) to give 1.62 g (65%) of chelate **5b**, m.p. 236—237 °C. Found (%): C, 68.62; H, 4.86; N, 6.81. $C_{24}H_{20}BF_3N_2O$. Calculated (%): C, 68.57; H, 4.76; N, 6.66. IR ($CHCl_3$, ν/cm^{-1}): 3380 (NH); 3370 (NH); 1655 (CO). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.23 (s, 3 H, Me); 6.51 (br.s, 1 H, NH); 6.87 (br.s, 1 H, NH); 7.15—7.60 (m, 15 H, 3Ph).

3-Acetyl-4-amino-2-trifluoromethylpyridine (7a). A mixture of 0.42 g (1.17 mmol) of **5a** and 0.28 g (2.34 mmol) of DMF DMA was refluxed in benzene for 6 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a column with SiO_2 (eluent $CHCl_3$) to obtain 0.35 g of chelate **6a*** containing a minor impurity of starting **5a**. This product was refluxed for 8 h with 10 ml of BuOH. After the BuOH was distilled off under reduced pres-

* To be identified, **6a** was recrystallized twice from a benzene—hexane (1 : 2) mixture, m.p. 188—189 °C. Found (%): C, 63.94; H, 5.61. $C_{22}H_{23}BF_3N_3O$. Calculated (%): C, 64.03; H, 5.39. IR (KBr, ν/cm^{-1}): 3390 (NH); 1670 (CO). Mass spectrum, *m/z*: 336 $[M-Ph]^+$. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 2.22 (t, 3 H, Me); 3.0 (br.s, 6 H, Me_2N), 5.23 (d, 1 H, CH, *J* = 13); 6.11 (s, 1 H, NH); 6.37 (s, 1 H, NH); 7.08 (d, 1 H, NCH, *J* = 13); 7.20—7.40 (m, 10 H, 2 Ph).

sure, the residue was chromatographed on a column with SiO_2 (eluent: C_6H_6 first, followed by $CHCl_3$) to isolate 0.126 g (52.5%) of pyridine **7a**, m.p. 168—169 °C that was purified by sublimation *in vacuo* at 80—90 °C and 1—2 Torr. Found (%): C, 47.06; H, 3.45. $C_8H_7F_3N_2O$. Calculated (%): C, 46.60; H, 3.51. IR ($CHCl_3$, ν/cm^{-1}): 3500 (NH); 1705 (CO). Mass-spectrum, *m/z*: 204 $[M]^+$.

4-Amino-3-benzoyl-2-trifluoromethylpyridine (7b). A mixture of 0.7 g (1.66 mmol) of **5b** and 0.25 g (2.15 mmol) of DMF DMA was refluxed in 10 ml of toluene for 15 h. The solvent was distilled off under reduced pressure, and the residue was purified on a column with SiO_2 (eluent — benzene). BuOH (10 ml) was added to the crude chelate **6b** (oil) thus obtained and the mixture was refluxed for 15 h. After the BuOH was distilled off under reduced pressure, the residue was recrystallized from a benzene — hexane (1:3) mixture to obtain 0.18 g of aminopyridine **7b**. Additionally, 0.09 g of **7b** were isolated from the mother liquor by column chromatography (SiO_2, eluent: benzene — acetone, 5 : 1). Total yield of **7b** was 0.27 g (47%), m.p. 162—163 °C. Found (%): C, 58.14; H, 3.55; N, 9.98. $C_{13}H_9F_3N_2O$. Calculated (%): C, 58.64; H, 3.38; N, 10.53. IR ($CHCl_3$, ν/cm^{-1}): 3500 and 3400 (NH_2); 1665 (CO). Mass spectrum, *m/z*: 266 $[M]^+$. ^1H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 4.50 (br.s, 2 H, NH_2); 6.79 (d, 1 H, H-5, J = 5.5); 7.52—7.85 (m, 5 H, Ph); 8.40 (d, 1 H, H-6, J = 5.5). ^{13}C NMR ($CDCl_3$, δ, ppm, *J*/Hz): 112.51 (d, C-5, ^1J = 163); 121.54 (q, CF_3, $^1J_{C,F}$ = 276); 118.88 (s, C-3); 128.99; 129.42; 134.56; 136.73 (Ph); 145.28 (q, C-2, $^2J_{C,F}$ = 34); 149.86 (d, C-6, ^1J = 181); 151.92 (d, C-4, ^2J = 7.6); 194.67 (CO).

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