

Reactions of β -methoxyvinyl trifluoromethyl ketones with 2-pyridinecarboxamidrazone

A convenient route to trifluoromethylated 4,5-dihydro-1*H*-1-picolinoylpyrazole hydrochlorides

Helio G. Bonacorso^{*}, Hilario Lewandowski, Roberta L. Drekenner, Michelle B. Costa, Claudio M.P. Pereira, Arci D. Wastowski, Clóvis Peppe, Marcos A.P. Martins, Nilo Zanatta

Núcleo de Química de Heterociclos—NUQUIMHE, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

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Abstract

A new series of six 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1*H*-1-picolinoylpyrazole hydrochlorides were synthesised in one-step in high yields by the reaction of β -methoxyvinyl trifluoromethyl ketones with 2-pyridinecarboxamidrazone in the presence of hydrochloric acid. The hydrochloride salts were easily converted to the respective new series of free trifluoromethylated 4,5-dihydro-1*H*-1-picolinoylpyrazoles using triethylamine in anhydrous diethyl ether. X-ray structure and ³⁵Cl NMR data from the pyrazole hydrochlorides are reported. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Enones; Amidrazones; Pyrazoles; Hydrochlorides; ³⁵Cl NMR

1. Introduction

A growing interest in the use of β -alkoxyvinyl trifluoromethyl ketones **1** to provide a wide range of trifluorinated heterocycles and acyclic compounds is evident from the large number of publications which have appeared in the past couple of years from different research groups [1–11]. In particular, the synthetic potential of compounds **1** to obtain series of novel heterocycles of five [12], six [13], seven membered rings [14], and more recently bi-heterocyclic compounds [15] has been reported by our group. Amidrazones also have been shown to be important precursors for many useful compounds, which have industrial and medicinal applications [16]. In the last decade, Mamolo and co-workers [17] have described the synthesis and antimycobacterial activity of some 2-pyridinecarboxamidrazones and their heterocyclic derivatives. Recently, some 4,5-dihydro-1*H*-pyrazole derivatives have been described for their antibacterial [18–21] and antifungal activities [21,22]. More specifically, a series of 5-aryl-1-isonicotinoyl-3-(pyridin-2-yl)-4,5-dihydro-1*H*-pyrazole derivatives [23] have been synthesized and their

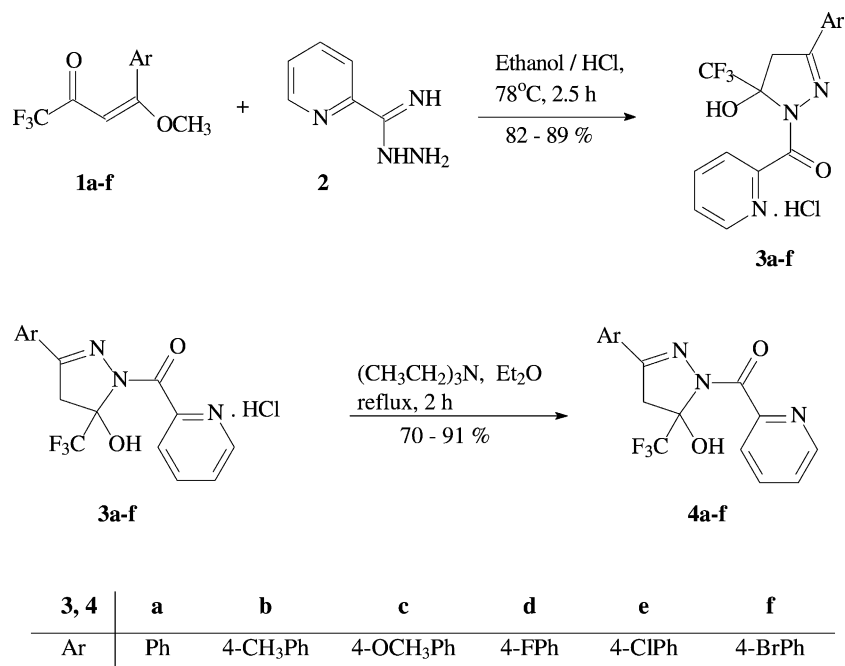
antimycobacterial activity evaluated toward a strain of *M. tuberculosis* H₃₇Rv and *M. tuberculosis* H₄, isolated from human bronchial aspirates. These heterocyclic compounds have exhibited interesting in vitro antimycobacterial activity against strains of *M. tuberculosis*. The above related pyridylpyrazoles [23] have been obtained from the reaction of the appropriate aromatic aldehyde and acetylpyridine, but in a three step reaction and in low yields, which involved an aldol condensation, cyclo-condensation with hydrazine and N-acylation with isonicotinoyl chloride.

Considering the important applications of β -alkoxyvinyl trifluoromethyl ketones **1**, amidrazones and pyridyl-1*H*-pyrazoles summarized above, we wish to report the facile synthesis of a new series of 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1*H*-1-picolinoylpyrazoles (**3**, **4**) from the direct cyclocondensation reaction of β -methoxy- β -aryl- α,β -unsaturated trifluoromethyl ketones **1a–f** with **2**.

2. Results and discussion

The synthesis of 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1*H*-1-picolinoylpyrazole hydrochlorides (**3a–f**) was carried out in ethanol in the presence of hydrochloric

^{*} Corresponding author. Fax: +55-55-220-8031.
E-mail address: heliogb@base.ufsm.br (H.G. Bonacorso).



Scheme 1.

acid. The reactions were monitored by TLC and the optimal reaction time and the temperature were 2.5 h at 78 °C, (Scheme 1). 3-Aryl-5-trifluoromethyl-1*H*-1-picolinoylpyrazole (**4a–f**) were easily obtained by addition of triethylamine to equimolar amounts of **3a–f**. The mixtures were stirred at reflux for 2 h, using diethyl ether as solvent (Scheme 1). The most satisfactory yields of the reactions, selected physical and NMR spectral data are presented in the experimental part and in Tables 1–4.

According to the procedure employed in this work, it is observed that β-alkoxyvinyl trifluoromethyl ketones **1** react with 2-pyridylcarboxamidine in the presence of hydrochloric acid leading to 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1*H*-1-picolinoylpyrazole hydrochlorides (**3a–f**).

Despite three reactive nitrogens in amidrazone **2**, this compound reacted specifically as a 1,2-dinucleophile. Subsequent in situ hydrolysis of the imine intermediate to carbonyl provided a picolinoyl group on 4,5-dihydropyrazoles in a single step reaction. Furthermore, compounds **3a–f** were obtained as hydrochloride derivatives which are convenient compounds for biological tests due to their potential activity combined with the desired water solubility. Hydrochlorides **3a–f** were converted in the respective new series of free 5-trifluoromethyl-4,5-dihydro-1*H*-picolinoylpyrazoles **4a–f** by treating the hydrochloride salts **3a–f** with triethylamine in anhydrous diethyl ether. In order to isolate the products **4a–f** easily from the triethylamine hydrochloride by a simple filtration, the use of anhydrous diethyl ether was required.

Table 1
Selected physical and ³⁵Cl NMR spectral data of hydrochlorides **3a–f**

Compound	Yield ^a (%)	Melting point (°C) ^b	Molecular formula (g/mol)	MS <i>m/z</i> ^c (%)	³⁵ Cl NMR δ (ppm)
3a	86	189–192	C ₁₆ H ₁₃ ClF ₃ N ₃ O ₂ (371.74)	334 (<i>M</i> ⁺ , 51), 224 (54), 266 (21), 106 (43), 78 (100)	–29.0
3b	82	201–203	C ₁₇ H ₁₅ ClF ₃ N ₃ O ₂ (385.77)	348 (<i>M</i> ⁺ , 63), 280 (31), 238 (65), 106 (51), 78 (100)	–29.0
3c	85	182–185	C ₁₇ H ₁₅ ClF ₃ N ₃ O ₃ (401.77)	365 (<i>M</i> ⁺ , 44), 296 (50), 254 (56), 106 (59), 78 (100)	–29.5
3d	86	191–194	C ₁₆ H ₁₂ ClF ₄ N ₃ O ₂ (389.73)	352 (<i>M</i> ⁺ , 35), 284 (34), 242 (65), 106 (51), 78 (100)	–20.0
3e	88	199–202	C ₁₆ H ₁₂ Cl ₂ F ₃ N ₃ O ₂ (406.19)	368 (<i>M</i> ⁺ , 28), 300 (23), 258 (50), 106 (49), 78 (100)	–29.4
3f	89	204–207	C ₁₆ H ₁₂ BrClF ₃ N ₃ O ₂ (450.64)	414 (<i>M</i> ⁺ , 19), 344 (15), 302 (31), 106 (50), 78 (100)	–29.5

^a Yields of isolated compounds.

^b The melting points are uncorrected.

^c Molecular ion resulted from dehydrochlorination.

Table 2
Selected ^1H and ^{13}C NMR spectral data^a of **3a–f**

Product	^1H -NMR, δ (ppm), J (Hz)/ ^{13}C -NMR, δ (ppm), J (Hz)
3a	8.77 (m, 1H, Py), 8.24 (m, 1H, Py), 7.92 (m, 1H, Py), 7.78 (m, 1H, Py), 7.60–7.35(m, 5H, Ph), 3.95 (d, 1H, $J_{\text{H4a-H4b}} = 19.1$, H4a), 3.78 (d, 1H, $J_{\text{H4b-H4a}} = 19.1$, H4b), 163.0 (C=O), 153.6 (C-3), 150.5; 146.6; 140.5; 126.3; 124.7 (Py), 129.8; 129.1; 129.0; 126.9 (Ph), 123.8 (q, $^1J_{\text{C-F}} = 285.4$, CF ₃), 92.3 (q, $^2J_{\text{C-F}} = 34.0$, C-5), 44.1 (C-4).
3b	8.73 (m, 1H, Py), 8.15 (m, 1H, Py), 7.84–7.20 (m, 2H, Py/4H, Ph), 3.94 (d, 1H, $J_{\text{H4a-H4b}} = 19.1$, H4a), 3.71 (d, 1H, $J_{\text{H4b-H4a}} = 19.1$, H4b), 2.30 (s, 3H, CH ₃), 163.9 (C=O), 152.8 (C-3), 151.9; 147.2; 140.6; 126.4; 123.1 (Py), 138.5; 129.4; 127.3; 126.7 (Ph), 123.1 (q, $^1J_{\text{C-F}} = 286.0$, CF ₃), 91.8 (q, $^2J_{\text{C-F}} = 34.0$, C-5), 44.0 (C-4), 20.8 (CH ₃).
3c	8.87 (m, 1H, Py), 8.27 (m, 1H, Py), 7.98–7.11 (m, 2H, Py/4H, Ph), 4.09 (d, 1H, $J_{\text{H4a-H4b}} = 18.9$, H4a), 3.95 (d, 1H, $J_{\text{H4b-H4a}} = 18.9$, H4b), 3.94 (s, 3H, OCH ₃), 161.5 (C=O), 161.8 (Ph), 153.7 (C-3), 128.7; 122.2; 114.5 (Ph), 149.4; 145.9; 141.8; 127.0; 125.3 (Py), 123.3 (q, $^1J_{\text{C-F}} = 285.1$, CF ₃), 92.3 (q, $^2J_{\text{C-F}} = 34.1$, C-5), 55.5 (OCH ₃), 44.1 (C-4).
3d	8.71 (m, 1H, Py), 8.10 (m, 1H, Py), 7.78–6.73 (m, 2H, Py e 4H Ph), 3.99 (d, 1H, $J_{\text{H4a-H4b}} = 19.2$, H4a), 3.72 (d, 1H, $J_{\text{H4b-H4a}} = 19.2$, H4b), 163.6 (d, $^1J_{\text{C-F}} = 249.2$, Ph), 163.1 (C=O), 152.5 (C-3), 150.7; 146.7; 140.1; 126.3; 124.4 (Py); 129.2 (d, $^3J_{\text{C-F}} = 8.8$, Ph), 126.5 (d, $^4J_{\text{C-F}} = 3.0$, Ph), 115.9 (d, $^2J_{\text{C-F}} = 22.0$, Ph), 123.5 (q, $^1J_{\text{C-F}} = 285.1$, CF ₃), 92.3 (q, $^2J_{\text{C-F}} = 34.0$, C-5), 44.1 (C-4).
3e	8.70 (m, 1H, Py), 8.06 (m, 1H, Py), 7.96–7.10 (m, 2H, Py/4H, Ph), 3.98 (d, 1H, $J_{\text{H4a-H4b}} = 19.2$, H4a), 3.69 (d, 1H, $J_{\text{H4b-H4a}} = 19.2$, H4b), 164.5 (C=O), 152.3 (C-3), 151.9; 147.8; 138.2; 125.5; 123.4 (Py), 135.4; 128.9; 128.8; 128.4 (Ph), 123.4 (q, $^1J_{\text{C-F}} = 285.7$, CF ₃), 91.9 (q, $^2J_{\text{C-F}} = 34.0$, C-5), 44.0 (C-4).
3f	8.69 (m, 1H, Py), 8.07 (m, 1H, Py), 7.75–7.13 (m, 2H, Py/4H, Ph) 3.97(d, 1H, $J_{\text{H4a-H4b}} = 19.2$, H4a), 3.70 (d, 1H, $J_{\text{H4b-H4a}} = 19.2$, H4b), 165.1 (C=O), 152.9 (C-3) 151.9; 148.2; 1377; 1319; 123.2 (Py), 129.2; 128.6; 125.4; 124.3 (Ph), 123.2 (q, $^1J_{\text{C-F}} = 285.6$, CF ₃), 92.1 (q, $^2J_{\text{C-F}} = 34.0$, C-5), 44.1 (C-4).

^a The NMR spectra were recorded on a Bruker DPX-200.13 MHz (^1H at 200.13 MHz and ^{13}C at 50.32 MHz) in DMSO- d_6 /TMS.

Table 3
Selected physical data of pyrazoles **4a–f**

Compound	Yield ^a (%)	Melting point ($^{\circ}\text{C}$) ^b	Molecular formula (g/mol)	MS m/z (%)
4a	75	66–69	C ₁₆ H ₁₂ F ₃ N ₃ O ₂ (335.29)	334 (M^+ , 21), 266 (14), 224 (36), 106 (35), 78 (100) 51(29)
4b	82	48–52	C ₁₇ H ₁₄ F ₃ N ₃ O ₂ (349.31)	348 (M^+ , 20), 280 (14), 238 (35), 106 (36), 78 (100) 51(21)
4c	91	39–42	C ₁₇ H ₁₄ F ₃ N ₃ O ₃ (365.31)	364 (M^+ , 15), 296 (30), 254 (37), 106 (48), 78 (100) 51(26)
4d	84	131–134	C ₁₆ H ₁₁ F ₄ N ₃ O ₂ (353.28)	352 (M^+ , 10), 284 (16), 242 (34), 106 (37), 78 (100) 51(25)
4e	72	80–83	C ₁₆ H ₁₁ ClF ₃ N ₃ O ₂ (369.73)	368 (M^+ , 7), 300 (12), 258 (24), 106 (38), 78 (100), 51(25)
4f	70	85–88	C ₁₆ H ₁₁ BrF ₃ N ₃ O ₂ (414.18)	414 (M^+ , 6), 344 (7), 302 (13), 106 (37), 78 (100), 51(22)

^a Yields of isolated compounds.

^b The melting points are uncorrected.

Table 4
Selected ^1H and ^{13}C NMR spectral data^a of **4a–f**

Product	^1H -NMR, δ (ppm), J (Hz)/ ^{13}C -NMR, δ (ppm), J (Hz)
4a	8.65 (m, 1H, Py), 8.46 (s, OH), 7.96 (m, 1H, Py), 7.60–7.41 (m, 2H, Py/5H, Ph), 3.98 (d, 1H, $J_{\text{H4a-H4b}} = 19.0$, H4a), 3.62 (d, 1H, $J_{\text{H4b-H4a}} = 19.0$, H4b), 165.8 (C=O), 153.9 (C-3), 152.3; 148.7; 136.7; 124.9; 122.7 (Py), 130.7; 129.9; 128.8; 126.5 (Ph), 123.3 (q, $^1J_{\text{C-F}} = 285.6$, CF ₃), 91.8 (q, $^2J_{\text{C-F}} = 33.9$, C-5), 44.2 (C-4).
4b	8.64 (m, 1H, Py), 8.42 (s, OH), 7.95 (m, 1H, Py), 7.59–7.20 (m, 2H, Py/4H, Ph), 3.94 (d, 1H, $J_{\text{H4a-H4b}} = 19.0$, H4a), 3.59 (d, 1H, $J_{\text{H4b-H4a}} = 19.0$, H4b), 2.31 (s, 3H, CH ₃), 165.7 (C=O), 153.9 (C-3), 152.2; 148.6; 136.6; 124.8; 122.6 (Py), 140.6; 129.3; 127.1; 126.4 (Ph), 123.3 (q, $^1J_{\text{C-F}} = 283.4$, CF ₃), 91.6 (q, $^2J_{\text{C-F}} = 33.3$, C-5), 44.3 (C-4), 20.9 (CH ₃).
4c	8.63 (m, 1H, Py), 8.38 (s, OH), 7.98–7.49(m, 1H Py/4H, Ph), 6.96 (d, 1H, Py), 3.92 (d, 1H, $J_{\text{H4a-H4b}} = 19.0$, H4a), 3.57 (d, 1H, $J_{\text{H4b-H4a}} = 19.0$, H4b), 3.77 (s, 3H, OCH ₃), 165.6 (C=O), 161.2 (Ph), 154.0 (C-3), 152.0; 148.7; 136.7; 124.8; 122.7 (Py), 128.3; 122.4; 114.2 (Ph), 123.3 (q, $^1J_{\text{C-F}} = 284.8$, CF ₃), 91.6 (q, $^2J_{\text{C-F}} = 33.6$, C-5), 55.3 (OCH ₃), 44.4 (C-4).
4d	8.64 (m, 1H, Py), 8.48 (s, OH), 7.96 (m, 1H,Py), 7.66–7.56(m, 1H, Py/4H, Ph), 7.29 (t, 1H, Py), 3.99 (d, 1H, $J_{\text{H4a-H4b}} = 19.2$, H4a), 3.62 (d, 1H, $J_{\text{H4b-H4a}} = 19.2$, H4b), 165.7(C=O), 163.4 (d, $^1J_{\text{C-F}} = 247.2$, Ph), 153.7 (C-3), 151.4 (d, $^4J_{\text{C-F}} = 0.7$, Ph), 148.6; 129.0; 128.8; 124.9; 122.6 (Py), 126.5 (d, $^3J_{\text{C-F}} = 3.4$, Ph), 115.8 (d, $^2J_{\text{C-F}} = 21.7$, Ph), 123.2 (q, $^1J_{\text{C-F}} = 284.0$, CF ₃), 91.8 (q, $^2J_{\text{C-F}} = 33.4$, C-5), 44.2 (C-4).
4e	8.64 (m, 1H, Py), 8.48 (s, OH), 7.98 (m, 1H, Py), 7.60–7.46 (m, 2H, Py/4H, Ph), 3.98 (d, 1H, $J_{\text{H4a-H4b}} = 19.2$, H4a), 3.61 (d, 1H, $J_{\text{H4b-H4a}} = 19.2$, H4b), 166.1 (C=O), 155.1 (C-3), 151.7; 149.0; 137.0; 125.3; 123.0 (Py), 135.7; 129.2; 129.2; 126.4 (Ph), 123.5 (q, $^1J_{\text{C-F}} = 283.8$, CF ₃), 92.3 (q, $^2J_{\text{C-F}} = 34.2$, C-5), 44.5 (C-4).
4f	8.65 (m, 1H, Py), 8.51 (s, OH), 7.96 (m, 1H, Py), 7.65–7.48(m, 2H, Py/4H, Ph), 3.99 (d, 1H, $J_{\text{H4a-H4b}} = 19.0$, H4a), 3.62 (d, 1H, $J_{\text{H4b-H4a}} = 19.0$, H4b), 165.5 (C=O), 153.5 (C-3), 151.2; 148.4; 136.4; 123.9; 122.4 (Py), 131.5; 128.9; 128.2; 124.7 (Ph), 123.1 (q, $^1J_{\text{C-F}} = 284.5$, CF ₃), 91.7 (q, $^2J_{\text{C-F}} = 33.8$, C-5), 43.8 (C-4).

^a The NMR spectra were recorded on a Bruker DPX-200.13 MHz (^1H at 200.13 MHz and ^{13}C at 50.32 MHz) in DMSO- d_6 /TMS.

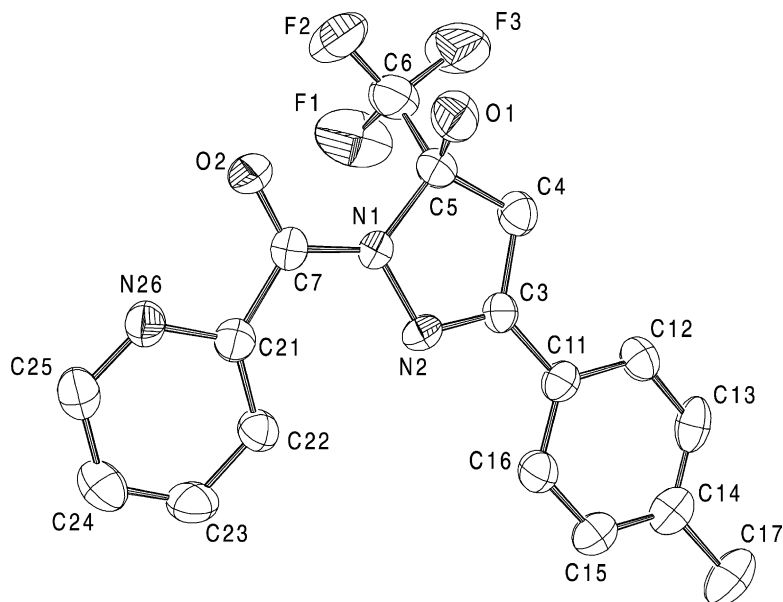


Fig. 1. ORTEP representation of cation **3b**. Bond distances (Å): N(1)–N(2) 1.403(5); N(1)–C(5) 1.490(6); N(1)–C(7) 1.356(6); N(2)–C(3) 1.278(5); C(3)–C(4) 1.492(6); C(3)–C(11) 1.452(6); C(4)–C(5) 1.528(6); C(5)–O(1) 1.429(7); C(5)–C(6) 1.521(8); C(6)–F(1) 1.329(7); C(6)–F(2) 1.310(6); C(6)–F(3) 1.331(6); C(7)–O(2) 1.218(5); C(7)–C(21) 1.512(7).

The melting point range of the aryl derivatives **3a–f** (salts) and **4a–f** are within 182–207 and 48–134 °C, respectively. The crystal structure of the pyrazole hydrochloride **3b** was confirmed by single crystal X-ray analysis (Fig. 1) [24].

In addition, we have attempted to prepare the aromatic pyrazole from dehydration reactions of **4a** using sulfuric acid [12c], sulfuric acid/dichloromethane [15a] or P₂O₅/chloroform [1] under various conditions, but all efforts failed. Our experiments show that the picolinoyl and trifluoromethyl groups on position 1 and 5 of the pyrazolines **4** act as strong protective groups with electron withdrawing effects that hinder the elimination of water and the subsequent aromatization of the five-membered ring.

3. Conclusion

In conclusion, this work describes a single and useful method for the synthesis of new picolinoyl-pyrazole hydrochlorides under mild conditions and in high yields. Particularly notable is the regiospecificity of the reaction between β -alkoxyvinyl trifluoromethyl ketones **1** and 2-pyridinecarboxamidrazone. These new compounds should be interesting for their potential biological activities and further synthetic transformations.

4. Experimental

Unless otherwise indicated all common reagents and solvents were used as obtained from commercial suppliers without further purification. All melting points were

determined on a Reichert Thermovar apparatus and are uncorrected. ¹H and ¹³C NMR spectra were acquired on a Bruker DPX 200 spectrometer (¹H at 200.13 MHz and ¹³C at 50.32 MHz), 5 mm sample tubes, 298 K, digital resolution ± 0.01 ppm, in DMSO-d₆ for **3**, **4a–f** using TMS as internal reference. ³⁵Cl NMR spectra were acquired on a Bruker DPX 400 spectrometer at 39.20 MHz, in 0.5 M solution of DMSO-d₆ for **3a–f** using KClO₄ (1007.0 ppm) and NaCl (0.0 ppm) as external reference. Mass spectra were registered in a HP 6890 GC connected to a HP 5973 MSD and interfaced by a Pentium PC. The GC was equipped with a split-splitless injector, autosampler, cross-linked HP-5 capillary column (30 m, 0.32 mm of internal diameter), and the helium was used as

Table 5

Supplementary data: elemental analyses^a of compounds **3**, **4a–f**

Compounds	Analysis (%) calculated			Analysis (%) found		
	C	H	N	C	H	N
3a	51.70	3.52	11.30	51.48	3.49	11.46
3b	52.93	3.92	10.89	52.83	3.77	11.03
3c	50.82	3.76	10.46	50.74	3.60	10.48
3d	49.31	3.10	10.78	49.28	3.05	10.94
3e	47.31	2.98	10.34	47.24	2.88	10.40
3f	42.64	2.68	9.32	42.68	2.70	9.33
4a	57.32	3.61	12.53	57.03	3.82	12.48
4b	58.45	4.04	12.03	58.21	4.22	12.27
4c	55.89	3.86	11.50	55.70	3.63	11.44
4d	54.40	3.14	11.89	54.61	3.38	11.98
4e	51.98	3.00	11.37	52.08	3.01	11.68
4f	46.40	2.68	10.15	46.33	2.61	9.93

^a The CHN elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyser (São Paulo University, USP, Brazil).

the carrier gas. The CHN elemental analyses were performed on a Perkin-Elmer 2400, CHN elemental analyser (São Paulo University, USP, Brazil) (Table 5).

4.1. Synthesis of 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1H-1-picolinoylpyrazole hydrochlorides **3a–f**: general procedure

In a 50 ml flask a mixture of 2 mmol of 4-aryl-4-methoxy-1,1,1-trifluoro-3-buten-2-one (**1a–f**) and 0.30 g (2 mmol) of 2-pyridylcarboxamidrazone (**2**) in 5 ml of anhydrous ethanol was magnetically stirred and warmed for 30 min at 50 °C. Subsequently, hydrochloric acid 36% (3.5 ml) was added slowly at the same temperature (50 °C) and the mixture stirred for 2 h at reflux. After cooling (10–15 °C), anhydrous diethyl ether (10 ml) was added and the solid **3** was collected by filtration. The crude product **3** was purified by recrystallization from a mixture of methanol/water 3:1.

4.2. Synthesis of 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1H-1-picolinoylpyrazoles **4a–f**: general procedure

In a 50 ml flask a mixture of 1 mmol of 3-aryl-5-hydroxy-5-trifluoromethyl-4,5-dihydro-1H-1-picolinoylpyrazole hydrochloride (**3a–f**) and triethylamine (1 mmol) in 40 ml of anhydrous diethyl ether was magnetically stirred for 2 h at reflux. After cooling (10–15 °C), the triethylamine hydrochloride was filtered off. The solvent was evaporated under reduced pressure and the crude product **4** purified by recrystallization from a mixture of *n*-hexane/chloroform 2:1.

4.3. X-ray crystal structure determination of compound **3b**

Crystal data for $C_{17}H_{15}ClF_3N_3O_2$, **3b**: monoclinic $P2_1/n$, $a = 7.025(1)$ Å, $b = 17.018(4)$ Å, $c = 14.392(5)$ Å, $\beta = 100.05(3)^\circ$, $V = 1694.1(7)$ Å³, $Z = 4$. Bruker SMART CCD, Mo K α radiation ($\lambda = 0.71073$ Å), $T = 293(2)$ K, 3766 reflections measured, 2981 independent, 238 parameters. Structure solution and refinement: Shelxs97, Shelxl97 [24], $R1 = 0.0675$, $wR2 = 0.1360$. Further details have been deposited with the Cambridge Crystallographic Data Centre under the deposition number CCDC-197186.

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