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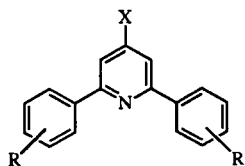
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1-Aryl-4,4,4-trifluoro-1,3-butanediones **1** react with β -amino- β -arylacrylonitrile **2**, readily available from acetonitrile with aryl nitriles in the presence of potassium *t*-butoxide, to afford the corresponding 2,6-diaryl-3-cyano-4-(trifluoromethyl)pyridines **3** in moderate to excellent yields.

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Introduction.

The development of efficient and selective synthesis of trifluoromethylated compounds has attracted increasing attention over the last several years, because they often bring about unique physiological properties [1]. Trifluoromethylated nitrogen-containing heterocycles, especially, are one of the most important compounds and are widely applied in the fields of medicinal [2] and agricultural [3] chemistry. Although a number of reports on the synthesis of these compounds appeared, there are scattered examples of functionalized pyridines carrying a trifluoromethyl group [4]. The yields and/or regioselectivity were not necessarily satisfactory. On the other hand, very recently, it was reported that some fluorine-containing 2,6-diarylpyridines showed potent herbicidal activity [5].



X = OMe, SMe R = CF₃, F, Cl

Figure. Structures of the 2,6-diarylpyridine herbicides.

As a further extension of our efforts on the synthesis of fluorine-containing pyridine derivatives [6], herein, we would like to describe our results on a facile synthesis of 2,6-diaryl-3-cyano-4-(trifluoromethyl)pyridines by a tandem Michael addition-cyclization reaction of trifluoromethyl-substituted β -diketones **1** with β -amino- β -arylacrylonitrile **2**.

Results and Discussion.

The starting trifluoromethyl-substituted β -diketones **1** could be readily prepared by the condensation of ethyl trifluoroacetate with methyl ketones as we have reported [6c]. The ¹H nmr analysis of **1** revealed that they have an extremely high enolic character (over 95%) due to the hydrogen bonding between the enolic hydroxyl group and a fluorine atom [7]. Enaminonitriles **2** were obtained in

excellent yields by the reaction of acetonitrile with aryl nitrile in the presence of potassium *t*-butoxide (Scheme 1, Table 1) [8].

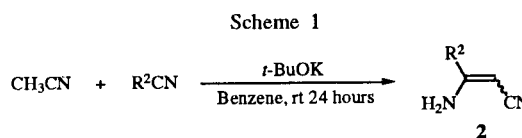


Table 1
Preparation of β -Amino- β -arylacrylonitriles **2**

Entry	R ²	Product	Isolated yield/%
1	Ph	2a	98
2	4-ClC ₆ H ₄	2b	97
3	4-MeOC ₆ H ₄	2c	90
4	4-FC ₆ H ₄	2d	98
5	4-CF ₃ C ₆ H ₄	2e	96
6	2-Pyridyl	2f	85

When **1a** was allowed to react with **2a** in ethanol at reflux temperature for 8 hours, 3-cyano-2,6-diphenyl-4-(trifluoromethyl)pyridine (**3a**) was obtained in 53% yield as a single regioisomer. The addition of a base, such as piperidine and potassium *t*-butoxide, resulted in lower yield of **3a** (28-35%). Employment of 1-propanol as a solvent caused the formation of by-products to reduce the yield of **3a** (48%). Both the prolonged reaction time (24 hours) and the use of two equivalents of **2a** were crucial to a high yield of the products (78%). The results of the reaction are summarized in Table 2, together with melting points and elemental analysis of **3**.

A variety of trifluoromethylated β -diketones **1b-e**, including a pyridyl or thienyl group, smoothly underwent a condensation reaction to give the corresponding 2,6-diaryl-4-(trifluoromethyl)pyridines **3** in moderate to good yields. Other aromatic β -aminoacrylonitriles **2b-e** participated well in the reaction with **1** affording good yields of the products, whereas the reaction with **2f** gave the complex mixture, along with fair yields of **3**, which were not improved at all in spite of the reaction time and tempera-

Scheme 2

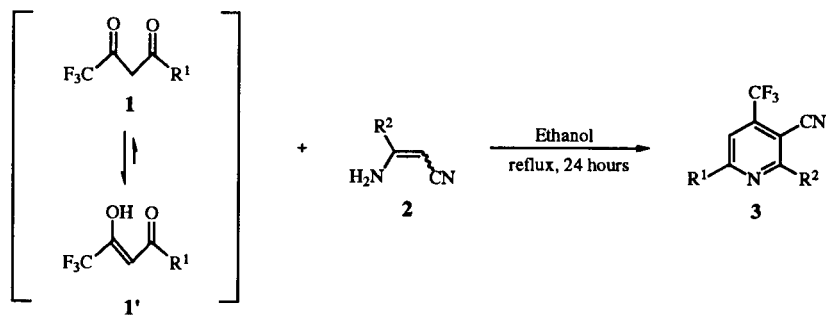
1a, R¹ = Ph1b, R¹ = 4-ClC₆H₄1c, R¹ = 4-MeOC₆H₄1d, R¹ = 2-Thienyl1e, R¹ = 2-Pyridyl

Table 2

Physical and Analytical Data of Compound 3

Compound No.	R ¹	R ²	Isolated yield/%	Mp/°C	Molecular formula	Elemental analysis (Calcd.)		
						C	H	N
3a	Ph	Ph	78	162-163	C ₁₉ H ₁₁ F ₃ N ₂	70.23 (70.37)	3.42 (3.42)	8.57 (8.64)
3b	4-ClC ₆ H ₄	Ph	79	156-157	C ₁₉ H ₁₀ ClF ₃ N ₂	63.63 (63.61)	2.83 (2.81)	7.82 (7.81)
3c	4-CH ₃ OC ₆ H ₄	Ph	53	169-170	C ₂₀ H ₁₃ F ₃ N ₂ O	67.61 (67.80)	3.63 (3.70)	7.87 (7.91)
3d	2-Thienyl	Ph	58	190-191	C ₁₇ H ₉ F ₃ N ₂ S	61.62 (61.81)	2.72 (2.75)	8.48 (8.48)
3e	2-Pyridyl	Ph	81	220-221	C ₁₈ H ₁₀ F ₃ N ₃	66.47 (66.46)	3.12 (3.10)	12.90 (12.92)
3f	Ph	4-ClC ₆ H ₄	70	164-164	C ₁₉ H ₁₀ ClF ₃ N ₂	63.74 (63.61)	2.85 (2.81)	7.85 (7.81)
3g	4-ClC ₆ H ₄	4-ClC ₆ H ₄	71	185-186	C ₁₉ H ₉ Cl ₂ F ₃ N ₂	58.18 (58.04)	2.37 (2.31)	7.13 (7.12)
3h	4-CH ₃ OC ₆ H ₄	4-ClC ₆ H ₄	49	205-206	C ₂₀ H ₁₂ ClF ₃ N ₂ O	61.69 (61.79)	3.15 (3.11)	7.17 (7.21)
3i	2-Thienyl	4-ClC ₆ H ₄	51	170-171	C ₁₇ H ₈ ClF ₃ N ₂ S	56.11 (55.98)	2.31 (2.21)	7.63 (7.68)
3j	2-Pyridyl	4-ClC ₆ H ₄	76	196-197	C ₁₈ H ₉ ClF ₃ N ₃	60.11 (60.10)	2.66 (2.52)	11.68 (11.68)
3k	Ph	4-CH ₃ OC ₆ H ₄	92	134-135	C ₂₀ H ₁₃ F ₃ N ₂ O	67.96 (67.80)	3.82 (3.70)	7.88 (7.91)
3l	4-ClC ₆ H ₄	4-CH ₃ OC ₆ H ₄	92	159-160	C ₂₀ H ₁₂ ClF ₃ N ₂ O	61.99 (61.79)	3.22 (3.11)	7.22 (7.21)
3m	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	77	162-163	C ₂₁ H ₁₅ F ₃ N ₂ O ₂	65.68 (65.62)	4.05 (3.93)	7.29 (7.29)
3n	2-Thienyl	4-CH ₃ OC ₆ H ₄	69	165-166	C ₁₈ H ₁₁ F ₃ N ₂ OS	59.79 (60.00)	3.05 (3.08)	7.73 (7.77)
3o	2-Pyridyl	4-CH ₃ OC ₆ H ₄	92	184-185	C ₁₉ H ₁₂ F ₃ N ₃ O	64.20 (64.23)	3.53 (3.40)	11.79 (11.83)
3p	Ph	4-FC ₆ H ₄	71	181-182	C ₁₉ H ₁₀ F ₄ N ₂	66.72 (66.67)	3.01 (2.94)	8.11 (8.18)
3q	4-ClC ₆ H ₄	4-FC ₆ H ₄	71	172-173	C ₁₉ H ₉ ClF ₄ N ₂	60.53 (60.57)	2.50 (2.41)	7.42 (7.44)
3r	4-CH ₃ OC ₆ H ₄	4-FC ₆ H ₄	44	180-181	C ₂₀ H ₁₂ F ₄ N ₂ O	64.37 (64.52)	3.30 (3.25)	7.46 (7.25)
3s	2-Thienyl	4-FC ₆ H ₄	43	196-197	C ₁₇ H ₈ F ₄ N ₂ S	58.42 (58.62)	2.41 (2.31)	7.96 (8.04)
3t	2-Pyridyl	4-FC ₆ H ₄	76	185-186	C ₁₈ H ₉ F ₄ N ₃	63.03 (62.98)	2.69 (2.64)	12.13 (12.24)

Table 2 (continued)
Physical and Analytical Data of Compound 3

Compound No.	R ¹	R ²	Isolated yield/%	Mp/°C	Molecular formula	Elemental analysis (Calcd.)		
						C	H	N
3u	Ph	4-CF ₃ C ₆ H ₄	58	196-197	C ₂₀ H ₁₀ F ₆ N ₂	61.42 (61.23)	2.70 (2.57)	7.14 (7.14)
3v	4-ClC ₆ H ₄	4-CF ₃ C ₆ H ₄	56	213-214	C ₂₀ H ₉ ClF ₆ N ₂	56.45 (56.29)	2.22 (2.13)	6.54 (6.56)
3w	4-CH ₃ OC ₆ H ₄	4-CF ₃ C ₆ H ₄	41	230-231	C ₂₁ H ₁₂ F ₆ N ₂ O	59.94 (59.72)	2.89 (2.86)	6.62 (6.63)
3x	2-Thienyl	4-CF ₃ C ₆ H ₄	35	215-216	C ₁₈ H ₈ F ₆ N ₂ S	54.31 (54.28)	2.19 (2.02)	7.00 (7.03)
3y	2-Pyridyl	4-CF ₃ C ₆ H ₄	54	196-197	C ₁₉ H ₉ F ₆ N ₃	57.88 (58.03)	2.43 (2.31)	10.66 (10.68)
3z	Ph	2-Pyridyl	27	155-156	C ₁₈ H ₁₀ F ₃ N ₃	66.45 (66.46)	3.16 (3.10)	12.72 (12.92)
3A	4-ClC ₆ H ₄	2-Pyridyl	27	170-171	C ₁₈ H ₉ ClF ₃ N ₃	60.08 (60.10)	2.56 (2.52)	11.59 (11.68)
3B	4-CH ₃ OC ₆ H ₄	2-Pyridyl	10	171-172	C ₁₉ H ₁₂ F ₃ N ₃ O	64.16 (64.23)	3.40 (3.40)	11.74 (11.83)
3C	2-Thienyl	2-Pyridyl	9	154-155	C ₁₆ H ₈ F ₃ N ₃ S	58.10 (58.00)	2.62 (2.43)	12.57 (12.68)
3D	2-Pyridyl	2-Pyridyl	30	205-206	C ₁₇ H ₉ F ₃ N ₄	62.66 (62.58)	2.87 (2.78)	17.19 (17.17)

ture being varied. A few comments of the effect of the substituents on the yields are worth noting. (1) The reaction of **1c,d** bearing a 4-methoxyphenyl or 2-thienyl group adjacent to a carbonyl carbon provided the corresponding pyridines **3** in lower yields than that of other aromatic substituents. (2) The use of nitrile **2c** having a 4-methoxyphenyl group at β -carbon afforded high yields of the product. On the basis of these results, it will be necessary for the high yields of **3** to carry an electron-withdrawing group on β -diketones **1** as well as an electron-releasing group on enamionitrile **2**. Of much significance is that the reaction of β -diketones **1** with nitriles **2** gave the corresponding 4-trifluoromethylated pyridines **3** exclusively, irrespective of the substituents of **1** or **2**. Their regiochemical assignment of **3** was made on the ¹³C and ¹⁹F nmr spectra noted in our previous report [6c].

In conclusion, the reaction of trifluoromethyl-substituted β -diketones **1** with β -amino- β -arylacrylonitrile **2** proceeded efficiently to give the corresponding 2,6-diaryl-4-trifluoromethylpyridines **3** in good yields. The present reaction will serve as a convenient and regioselective method for the synthesis of **3**, which is not conveniently obtained by other methods. Further studies on the agrochemical activities are in progress and will be disclosed in due course.

EXPERIMENTAL

Melting points were determined on a Yanagimoto MP-S2 micro melting point apparatus and are uncorrected. The ¹H and ¹³C nmr spectra were recorded on a JEOL α -400 instrument

with tetramethylsilane as an internal standard. The ¹⁹F nmr spectra were obtained on the same apparatus using trifluoroacetic acid as an external standard. The ir spectra were measured with a Perkin Elmer FT-IR 1640 spectrometer. The mass spectra were recorded with a Shimadzu QP-1000 instrument operating at ionization potential of 70 eV. Elemental analysis were performed on a Yanaco CHN Corder MT-3 elemental analyzer. All the commercially available reagents were used without further purification. 1-Aryl-4,4,4-trifluoro-1,3-butanediones **1** were prepared by a previously described procedure [7]. Starting materials **2** were obtained by the following procedure.

General Procedure for the Preparation of Enamionitriles **2**.

To a benzene (40 ml) solution of aryl nitrile (10 mmoles) and acetonitrile (20 mmoles) was added potassium *t*-butoxide (30 mmoles) at room temperature. After being stirred at room temperature for 24 hours, the resulting suspension was quenched with aqueous sodium bicarbonate (50 ml) and extracted with diethyl ether (50 ml). The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/benzene (1:5), followed by recrystallization from ethyl acetate/hexane (1:1). Compounds **2a-e** have been reported [9]. Physical and spectral data of **2f** are shown below.

3-Amino-3-(2-pyridyl)acrylonitrile (**2f**).

This compound had mp 118-119°; ¹H nmr (deuteriochloroform): δ 4.68 (s, 1H), 5.95 (br s, 2H), 7.38 (ddd, J = 7.8, 4.8, 1.0 Hz, 1H), 7.67 (ddd, J = 7.8, 1.0, 1.0 Hz, 1H), 7.78 (dt, J = 7.8, 1.8 Hz, 1H), 8.63 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H); ir (chloroform): 3500 (NH), 3381 (NH), 2195 (CN), 1618 (NH) cm⁻¹; ms: m/z 145 (100, M⁺), 118 (25), 105 (52), 79 (89).

Anal. Calcd. for C₈H₇N₃: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.32; H, 4.81; N, 28.72.

General Procedure for the Synthesis of 2,6-Diaryl-3-cyano-4-(trifluoromethyl)pyridines **3**.

To an ethanol (6 ml) solution of trifluoromethyl-substituted β -diketones **1** (3 mmoles) was added enamionitriles **2** (6 mmoles), and the mixture was stirred at reflux temperature for 24 hours. After removal of the solvent, the residue was purified by column chromatography on silica gel eluting with benzene/hexane (1:1) or ethyl acetate/hexane (1:4), followed by recrystallization from ethyl acetate/hexane (1:1). The melting points and elemental analysis of pyridines **3** are listed in Table 1. Other spectral data of **3** are shown below.

3-Cyano-2,6-diphenyl-4-(trifluoromethyl)pyridine (**3a**).

This compound had ^1H nmr (deuteriochloroform): δ 7.53-7.57 (m, 6H), 8.00-8.01 (m, 2H), 8.04 (s, 1H), 8.16-8.17 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.89 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 324 (58, M^+), 323 (100).

6-(4-Chlorophenyl)-3-cyano-2-phenyl-4-(trifluoromethyl)pyridine (**3b**).

This compound had ^1H nmr (deuteriochloroform): δ 7.52 and 8.12 (AB q, $J = 8.8$ Hz, 4H), 7.57-7.59 (m, 3H), 7.98-8.00 (m, 2H), 8.02 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.87 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 360 (23, M^+ +2), 358 (66, M^+), 357 (100).

3-Cyano-6-(4-methoxyphenyl)-2-phenyl-4-(trifluoromethyl)pyridine (**3c**).

This compound had ^1H nmr (deuteriochloroform): δ 3.88 (s, 3H), 7.02 and 8.14 (AB q, $J = 8.5$ Hz, 4H), 7.55-7.58 (m, 3H), 7.96 (s, 1H), 7.97-8.00 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.80 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 354 (100, M^+), 353 (88), 339 (28), 310 (39).

3-Cyano-2-phenyl-6-(2-thienyl)-4-(trifluoromethyl)pyridine (**3d**).

This compound had ^1H nmr (deuteriochloroform): δ 7.22 (dd, $J = 5.1, 3.8$ Hz, 1H), 7.55-7.58 (m, 3H), 7.60 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.83 (dd, $J = 3.8, 1.0$ Hz, 1H), 7.88 (s, 1H), 7.98-8.00 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.76 (s, 3F); ir (Nujol): 2221 (CN) cm^{-1} ; ms: m/z 330 (64, M^+), 329 (100).

3-Cyano-2-phenyl-6-(2-pyridyl)-4-(trifluoromethyl)pyridine (**3e**).

This compound had ^1H nmr (deuteriochloroform): δ 7.44 (ddd, $J = 7.8, 5.2, 1.2$ Hz, 1H), 7.58-7.59 (m, 3H), 7.89 (dt, $J = 7.8, 1.7$ Hz, 1H), 8.00-8.02 (m, 2H), 8.60 (ddd, $J = 7.8, 1.2, 0.87$ Hz, 1H), 8.76 (ddd, $J = 5.2, 1.7, 0.87$ Hz, 1H), 8.87 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 14.06 (s, 3F); ir (Nujol): 2227 (CN) cm^{-1} ; ms: m/z 325 (69, M^+), 324 (100).

2-(4-Chlorophenyl)-3-cyano-6-phenyl-4-(trifluoromethyl)pyridine (**3f**).

This compound had ^1H nmr (deuteriochloroform): δ 7.54 and 7.97 (AB q, $J = 8.5$ Hz, 4H), 7.55-7.56 (m, 3H), 8.06 (s, 1H), 8.15-8.17 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.87 (s, 3F); ir (Nujol): 2225 (CN) cm^{-1} ; ms: m/z 360 (23, M^+ +2), 358 (69, M^+), 357 (100).

2,6-Bis(4-chlorophenyl)-3-cyano-4-(trifluoromethyl)pyridine (**3g**).

This compound had ^1H nmr (deuteriochloroform): δ 7.53 and 8.12 (AB q, $J = 8.8$ Hz, 4H), 7.55 and 7.95 (AB q, $J = 8.8$ Hz,

4H), 8.04 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.91 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 396 (9, M^+ +4), 394 (52, M^+ +2), 392 (79, M^+), 391 (100), 357 (21).

2-(4-Chlorophenyl)-3-cyano-6-(4-methoxyphenyl)-4-(trifluoromethyl)pyridine (**3h**).

This compound had ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H), 7.04 and 8.14 (AB q, $J = 8.8$ Hz, 4H), 7.54 and 7.95 (AB q, $J = 8.4$ Hz, 4H), 7.98 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.79 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 390 (35, M^+ +2), 388 (100, M^+), 373 (22), 344 (26).

2-(4-Chlorophenyl)-3-cyano-6-(2-thienyl)-4-(trifluoromethyl)pyridine (**3i**).

This compound had ^1H nmr (deuteriochloroform): δ 7.21 (dd, $J = 5.0, 3.8$ Hz, 1H), 7.54 and 7.95 (AB q, $J = 8.4$ Hz, 4H), 7.62 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.83 (dd, $J = 3.8, 1.0$ Hz, 1H), 7.88 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.71 (s, 3F); ir (Nujol): 2221 (CN) cm^{-1} ; ms: m/z 366 (27, M^+ +2), 364 (70, M^+), 363 (100).

2-(4-Chlorophenyl)-3-cyano-6-(2-pyridyl)-4-(trifluoromethyl)pyridine (**3j**).

This compound had ^1H nmr (deuteriochloroform): δ 7.46 (ddd, $J = 7.6, 4.8, 0.67$ Hz, 1H), 7.56 and 7.97 (AB q, $J = 8.3$ Hz, 4H), 7.90 (dt, $J = 7.6, 1.6$ Hz, 1H), 8.57 (ddd, $J = 7.6, 0.86, 0.67$ Hz, 1H), 8.77 (ddd, $J = 4.8, 1.6, 0.86$ Hz, 1H), 8.88 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 14.00 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 361 (26, M^+ +2), 359 (73, M^+), 358 (100).

3-Cyano-2-(4-methoxyphenyl)-6-phenyl-4-(trifluoromethyl)pyridine (**3k**).

This compound had ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H), 7.07 and 8.03 (AB q, $J = 8.8$ Hz, 4H), 7.53-7.56 (m, 3H), 7.99 (s, 1H), 8.15-8.17 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.82 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 354 (81, M^+), 353 (100), 310 (39).

6-(4-Chlorophenyl)-3-cyano-2-(4-methoxyphenyl)-4-(trifluoromethyl)pyridine (**3l**).

This compound had ^1H nmr (deuteriochloroform): δ 3.91 (s, 3H), 7.08 and 8.01 (AB q, $J = 8.8$ Hz, 4H), 7.51 and 8.12 (AB q, $J = 8.5$ Hz, 4H), 7.96 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.88 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 390 (42, M^+ +2), 388 (100, M^+), 387 (98), 344 (28).

3-Cyano-2,6-bis(4-methoxyphenyl)-4-(trifluoromethyl)pyridine (**3m**).

This compound had ^1H nmr (deuteriochloroform): δ 3.89 (s, 3H), 3.90 (s, 3H), 7.04 and 8.15 (AB q, $J = 8.8$ Hz, 4H), 7.07 and 8.02 (AB q, $J = 8.8$ Hz, 4H), 7.91 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.87 (s, 3F); ir (Nujol): 2221 (CN) cm^{-1} ; ms: m/z 384 (100, M^+), 383 (86), 369 (24), 340 (22), 297 (16).

3-Cyano-2-(4-methoxyphenyl)-6-(2-thienyl)-4-(trifluoromethyl)pyridine (**3n**).

This compound had ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H), 7.07 and 8.02 (AB q, $J = 8.9$ Hz, 4H), 7.20 (dd, $J = 5.0, 3.9$ Hz, 1H), 7.60 (dd, $J = 5.0, 0.98$ Hz, 1H), 7.82 (dd, $J = 3.9, 0.98$ Hz, 1H), 7.82 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.60 (s,

3F); ir (Nujol): 2220 (CN) cm^{-1} ; ms: m/z 360 (100, M^+), 359 (98), 344 (15), 316 (29).

3-Cyano-2-(4-methoxyphenyl)-6-(2-pyridyl)-4-(trifluoromethyl)pyridine (3o).

This compound had ^1H nmr (deuteriochloroform): δ 3.92 (s, 3H), 7.09 and 8.06 (AB q, $J = 8.7$ Hz, 4H), 7.44 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1H), 7.89 (dt, $J = 7.7$, 1.7 Hz, 1H), 8.60 (ddd, $J = 7.7$, 1.1, 0.94 Hz, 1H), 8.76 (ddd, $J = 4.8$, 1.7, 0.94 Hz, 1H), 8.80 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 14.00 (s, 3F); ir (Nujol): 2226 (CN) cm^{-1} ; ms: m/z 355 (79, M^+), 354 (100), 311 (24).

3-Cyano-2-(4-fluorophenyl)-6-phenyl-4-(trifluoromethyl)pyridine (3p).

This compound had ^1H nmr (deuteriochloroform): δ 7.26 (dd, $J = 8.9$, 8.8 Hz, 2H), 7.52-7.58 (m, 3H), 8.04 (dd, $J = 8.8$, 4.9 Hz, 2H), 8.06 (s, 1H), 8.16-8.18 (m, 2H); ^{19}F nmr (deuteriochloroform): δ -31.39 (dd, $J = 8.9$, 4.9 Hz, 1F), 13.91 (s, 3F); ir (Nujol): 2224 (CN) cm^{-1} ; ms: m/z 342 (61, M^+), 341 (100).

6-(4-Chlorophenyl)-3-cyano-2-(4-fluorophenyl)-4-(trifluoromethyl)pyridine (3q).

This compound had ^1H nmr (deuteriochloroform): δ 7.26 (dd, $J = 9.6$, 8.5 Hz, 2H), 7.53 and 8.12 (AB q, $J = 8.5$ Hz, 4H), 8.02 (dd, $J = 8.5$, 4.2 Hz, 2H), 8.02 (s, 1H); ^{19}F nmr (deuteriochloroform): δ -31.06 (dd, $J = 9.6$, 4.2 Hz, 1F), 13.93 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 378 (25, $M^+ + 2$), 376 (66, M^+), 375 (100), 341 (15).

3-Cyano-2-(4-fluorophenyl)-6-(4-methoxyphenyl)-4-(trifluoromethyl)pyridine (3r).

This compound had ^1H nmr (deuteriochloroform): δ 3.90 (s, 3H), 7.04 and 8.14 (AB q, $J = 8.9$ Hz, 4H), 7.25 (dd, $J = 8.8$, 8.1 Hz, 2H), 7.97 (s, 1H), 8.02 (dd, $J = 8.8$, 4.9 Hz, 2H); ^{19}F nmr (deuteriochloroform): δ -32.14 (dd, $J = 8.1$, 4.9 Hz, 1F), 13.30 (s, 3F); ir (Nujol): 2220 (CN) cm^{-1} ; ms: m/z 372 (100, M^+), 371 (76), 357 (27), 328 (37).

3-Cyano-2-(4-fluorophenyl)-6-(2-thienyl)-4-(trifluoromethyl)pyridine (3s).

This compound had ^1H nmr (deuteriochloroform): δ 7.21 (dd, $J = 5.0$, 3.8 Hz, 1H), 7.25 (dd, $J = 8.9$, 8.2 Hz, 2H), 7.62 (dd, $J = 5.0$, 1.0 Hz, 1H), 7.83 (dd, $J = 3.8$, 1.0 Hz, 1H), 7.88 (s, 1H), 8.02 (dd, $J = 8.9$, 5.0 Hz, 2H); ^{19}F nmr (deuteriochloroform): δ -31.16 (dd, $J = 8.2$, 5.0 Hz, 1F), 13.74 (s, 3F); ir (Nujol): 2223 (CN) cm^{-1} ; ms: m/z 348 (65, M^+), 347 (100).

3-Cyano-2-(4-fluorophenyl)-6-(2-pyridyl)-4-(trifluoromethyl)pyridine (3t).

This compound had ^1H nmr (deuteriochloroform): δ 7.27 (dd, $J = 9.6$, 8.6 Hz, 2H), 7.46 (ddd, $J = 7.7$, 4.7, 0.89 Hz, 1H), 7.90 (dt, $J = 7.7$, 1.7 Hz, 1H), 8.04 (dd, $J = 8.6$, 4.1 Hz, 2H), 8.58 (ddd, $J = 7.7$, 0.89, 0.80 Hz, 1H), 8.77 (ddd, $J = 4.7$, 1.7, 0.80 Hz, 1H), 8.87 (s, 1H); ^{19}F nmr (deuteriochloroform): δ -31.36 (dd, $J = 9.6$, 4.1 Hz, 1F), 14.00 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 343 (80, M^+), 342 (100).

3-Cyano-6-phenyl-2-(4-trifluoromethylphenyl)-4-(trifluoromethyl)pyridine (3u).

This compound had ^1H nmr (deuteriochloroform): δ 7.54-7.60 (m, 3H), 7.84 and 8.13 (AB q, $J = 8.2$ Hz, 4H), 8.12 (s, 1H), 8.16-8.19 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 13.96 (s, 3F), 14.89 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 392 (80, M^+), 391 (100).

6-(4-Chlorophenyl)-3-cyano-2-(4-trifluoromethylphenyl)-4-(trifluoromethyl)pyridine (3v).

This compound had ^1H nmr (deuteriochloroform): δ 7.54 and 8.13 (AB q, $J = 8.8$ Hz, 4H), 7.85 and 8.11 (AB q, $J = 8.4$ Hz, 4H), 8.09 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.91 (s, 3F), 14.84 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 428 (26, $M^+ + 2$), 426 (77, M^+), 425 (100), 391 (22).

3-Cyano-6-(4-methoxyphenyl)-2-(4-trifluoromethylphenyl)-4-(trifluoromethyl)pyridine (3w).

This compound had ^1H nmr (deuteriochloroform): δ 3.91 (s, 3H), 7.05 and 8.16 (AB q, $J = 9.0$ Hz, 4H), 7.84 and 8.11 (AB q, $J = 8.1$ Hz, 4H), 8.04 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.90 (s, 3F), 14.94 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 422 (100, M^+), 421 (65), 407 (22), 378 (29).

3-Cyano-6-(2-thienyl)-2-(4-trifluoromethylphenyl)-4-(trifluoromethyl)pyridine (3x).

This compound had ^1H nmr (deuteriochloroform): δ 7.22 (dd, $J = 4.9$, 3.8 Hz, 1H), 7.64 (dd, $J = 4.9$, 1.1 Hz, 1H), 7.83 and 8.10 (AB q, $J = 8.2$ Hz, 4H), 7.86 (dd, $J = 3.8$, 1.1 Hz, 1H), 7.94 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 13.62 (s, 3F), 14.76 (s, 3F); ir (Nujol): 2229 (CN) cm^{-1} ; ms: m/z 398 (69, M^+), 397 (100).

3-Cyano-6-(2-pyridyl)-2-(4-trifluoromethylphenyl)-4-(trifluoromethyl)pyridine (3y).

This compound had ^1H nmr (deuteriochloroform): δ 7.47 (ddd, $J = 7.7$, 4.7, 1.0 Hz, 1H), 7.86 and 8.13 (AB q, $J = 8.3$ Hz, 4H), 7.91 (dt, $J = 7.7$, 1.6 Hz, 1H), 8.58 (dt, $J = 7.7$, 1.0 Hz, 1H), 8.78 (ddd, $J = 4.7$, 1.6, 1.0 Hz, 1H), 8.94 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 14.04 (s, 3F), 14.88 (s, 3F); ir (Nujol): 2228 (CN) cm^{-1} ; ms: m/z 393 (78, M^+), 392 (100).

3-Cyano-6-phenyl-2-(2-pyridyl)-4-(trifluoromethyl)pyridine (3z).

This compound had ^1H nmr (deuteriochloroform): δ 7.49 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1H), 7.55-7.58 (m, 3H), 7.94 (dt, $J = 7.7$, 1.7 Hz, 1H), 8.12 (s, 1H), 8.18-8.20 (m, 2H), 8.32 (ddd, $J = 7.7$, 1.1, 0.98 Hz, 1H), 8.84 (ddd, $J = 4.8$, 1.7, 0.98 Hz, 1H); ^{19}F nmr (deuteriochloroform): δ 13.96 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 325 (67, M^+), 324 (100).

6-(4-Chlorophenyl)-3-cyano-2-(2-pyridyl)-4-(trifluoromethyl)pyridine (3A).

This compound had ^1H nmr (deuteriochloroform): δ 7.50 (ddd, $J = 7.8$, 4.8, 1.1 Hz, 1H), 7.54 and 8.14 (AB q, $J = 8.8$ Hz, 4H), 7.95 (dt, $J = 7.8$, 1.7 Hz, 1H), 8.09 (s, 1H), 8.29 (ddd, $J = 7.8$, 1.1, 0.98 Hz, 1H), 8.84 (ddd, $J = 4.8$, 1.7, 0.98 Hz, 1H); ^{19}F nmr (deuteriochloroform): δ 13.91 (s, 3F); ir (Nujol): 2220 (CN) cm^{-1} ; ms: m/z 361 (25, $M^+ + 2$), 359 (71, M^+), 358 (100), 324 (17).

3-Cyano-6-(4-methoxyphenyl)-2-(2-pyridyl)-4-(trifluoromethyl)pyridine (3B).

This compound had ^1H nmr (deuteriochloroform): δ 3.91 (s, 3H), 7.05 and 8.16 (AB q, $J = 8.9$ Hz, 4H), 7.48 (ddd, $J = 7.8$, 4.9, 1.1 Hz, 1H), 7.93 (dt, $J = 7.8$, 1.7 Hz, 1H), 8.04 (s, 1H), 8.29 (ddd, $J = 7.8$, 1.1, 1.0 Hz, 1H), 8.82 (ddd, $J = 4.9$, 1.7, 1.0 Hz, 1H); ^{19}F nmr (deuteriochloroform): δ 13.76 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 355 (100, M^+), 354 (83), 340 (26), 311 (25).

3-Cyano-2-(2-pyridyl)-6-(2-thienyl)-4-(trifluoromethyl)pyridine (3C).

This compound had ^1H nmr (deuteriochloroform): δ 7.22 (dd, $J = 5.0$, 3.8 Hz, 1H), 7.48 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1H), 7.62 (dd, $J = 5.0$, 1.1 Hz, 1H), 7.84 (dd, $J = 3.8$, 1.1 Hz, 1H), 7.94 (dt, $J = 7.7$, 1.9 Hz, 1H), 7.95 (s, 1H), 8.27 (ddd, $J = 7.7$, 1.1, 1.0 Hz, 1H), 8.82 (ddd, $J = 4.8$, 1.9, 1.0 Hz, 1H); ^{19}F nmr (deuteriochloroform): δ 13.70 (s, 3F); ir (Nujol): 2222 (CN) cm^{-1} ; ms: m/z 331 (64, M^+), 330 (100).

3-Cyano-2,6-di(2-pyridyl)-4-(trifluoromethyl)pyridine (3D).

This compound had ^1H nmr (deuteriochloroform): δ 7.46 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1H), 7.50 (ddd, $J = 7.6$, 4.8, 1.0 Hz, 1H), 7.91 (dt, $J = 7.7$, 1.5 Hz, 1H), 7.96 (dt, $J = 7.6$, 1.5 Hz, 1H), 8.30 (ddd, $J = 7.6$, 1.0, 0.92 Hz, 1H), 8.61 (ddd, $J = 7.7$, 1.1, 0.92 Hz, 1H), 8.77 (ddd, $J = 4.8$, 1.5, 0.92 Hz, 1H), 8.85 (ddd, $J = 4.8$, 1.5, 0.92 Hz, 1H), 8.93 (s, 1H); ^{19}F nmr (deuteriochloroform): δ 14.04 (s, 3F); ir (Nujol): 2225 (CN) cm^{-1} ; ms: m/z 326 (78, M^+), 325 (100).

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