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SYNTHESIS OF 2-(PYRIDYLAZO)-2-FURYL- AND 2-(PYRIDYLAZO)-2-THIENYLMETHINES AND OTHER HETEROCYCLIC SCHIFF BASES IN THE PRESENCE OF MOLECULAR SIEVES

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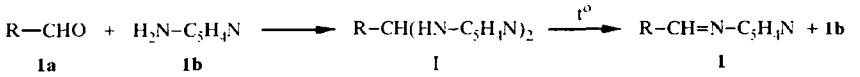
The reactions of 2-furaldehyde, 2-thiophenecarbaldehyde, and their 5-methyl derivatives with 2-aminopyridines and some other amines in the presence of molecular sieves as a dehydrating agent and acid catalyst have been studied. A series of new heterocyclic azomethines was synthesized. Proposals were made for the mechanism of the condensation involving 2-aminopyridines and the structure of the intermediates in these processes.

Keywords: heterocyclic Schiff bases, 2-pyridylazomethines, molecular sieves.

In a continuation of our previous work [1], we studied the reaction of 2-furaldehydes and 2-thiophenecarbaldehydes with a series of 2-aminopyridines and other amines in order to synthesize the corresponding azomethines, which are potential synthones and biologically active compounds as well as prochiral substrates.

The following physical characteristics have been reported for 2-(2-furfuryliden)aminopyridine (**1**): bp 114-116°C (1.3 mm), mp 54.5-55°C [2], bp 109-113°C (0.05 mm), mp 52-55°C [3]. The composition and structure of this compound were proven by elemental analysis and consecutive hydrogenation and alkylation at the C=N bond. However, the synthesis of this compound is a difficult problem. In a number of studies [4-6] and the rather recent work of Lukovkin [7], the product obtained in the reaction of furfural (**1a**) with 2-aminopyridine (**1b**) was mistakenly identified as **1** but in fact is N,N'-(2-furfurylidene)bis-2-aminopyridine (**I**). This is indicated by its high melting point (in the absence of other characteristics): 85 [4], 84-86 [5], 87.5 [6], and 95°C [7]. Jaye and Kogon [3] proposed that the primary product in the reaction of aldehyde **1a** and amine **1b** is aminal **I**, which is converted by subsequent thermal decomposition to **1**.



The following conclusion may be made concerning the methods for synthesis of imine **1** and its thiophene analog based on the literature data. The preparation of these compounds requires carrying out the condensation of the corresponding aldehyde with 2-aminopyridine at a high temperature (for example, in cumene [3] or toluene at reflux [8]) or in a non-aqueous acid such as HCO_2H or in the presence of an acid catalyst such as $POCl_3$ [9]. Thus, we assumed that the use of zeolites as a dehydrating and acid catalytic agent as in our previous work [1] would prove successful for achieving our present aims.

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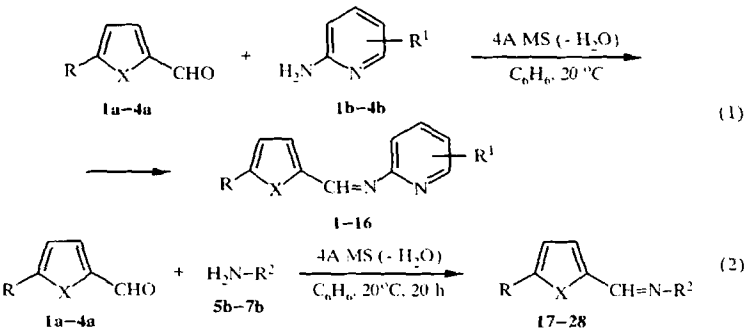
In the present work, we studied the reaction of 2-furaldehyde, 2-thiophenecarbaldehyde, and their 5-methyl derivatives (**1a-4a**) with 2-aminopyridine and its 3-, 4-, and 6-methyl derivatives (**1b-4b**) as well as with 3- and 4-trifluoromethylanilines (**5b, 6b**) and 1-phenylethylamine (**7b**). The reactions were carried out under the conditions used in our previous work [1], which are optimal for such condensations. The aldehyde and amine taken in equimolar amounts were dissolved in dry benzene and brand 4A molecular sieves (MS) (1 g per mmole reagent) were added. The reaction was carried out periodically taking probes analyzed by gas–liquid chromatography or GC/MS until the almost complete conversion of the starting substrates into the desired azomethines (Scheme 1).

Scheme 1



R = H, Me; R^1 = H, 3-Me, 4-Me, 6-Me; R^2 = 3-F_3C-C_6H_4, 4-F_3C-C_6H_4, Ph(Me)CH; X = O, S

Synthesis of heterocyclic Schiff bases in the presence of molecular sieves

After completion of the reaction, the molecular sieves were filtered off and benzene was distilled off on a rotary evaporator. The products were separated by vacuum distillation or recrystallization from benzene, petroleum ether, or their mixtures. These products are either crystalline or oily, white or light yellow compounds. The characteristics of the reactions and resulted azomethines (**1-28**) are given in Tables 1-3.

TABLE 1. Characteristics of Reaction (1) and Products **1-16**

Imine	X	R	R^1	Reaction time, h	mp, °C	Color	Yield*, %
1*[2]	O	H	H	19	52-53	White	81
2	O	H	3-CH_3	19	94-95/0.1 mm	Yellow	56
3	O	H	4-CH_3	23	82-83	White	91
4	O	H	6-CH_3	6	86-87/0.1 mm	Yellow	74
5	O	CH_3	H	20	96-97/0.1 mm	Yellow	66
6	O	CH_3	3-CH_3	21	97-98/0.1 mm	Yellow	63
7	O	CH_3	4-CH_3	23	48-49	Yellow	62
8	O	CH_3	6-CH_3	21	40-41 99-100/0.1 mm	Yellow	59
9*[3]	S	H	H	20	55-56	White	80
10	S	H	3-CH_3	23.5	106-107/0.1 mm	Yellow	71
11	S	H	4-CH_3	20	65-66	White	80
12	S	H	6-CH_3	23.5	45-46	Yellow	95
13	S	CH_3	H	17	64-65	Yellow	90
14	S	CH_3	3-CH_3	17	75-76	Yellow	89
15	S	CH_3	4-CH_3	22	39-40	Yellow	76
16	S	CH_3	6-CH_3	23	54-55	Yellow	96

*[2] Literature data are given in text.

*[3] Mp 54-56°C [8], bp 148°C/1.6 mm, mp 56-57°C [9].

TABLE. 2. Characteristics of Imines **17-28***

Imine	X	R	R^2	mp/bp, °C	Yield*[2], %
17	O	H	3-F_3C-C_6H_4	80-82/0.1 mm	79
18	O	H	4-F_3C-C_6H_4	70-71	70
19	O	H	Ph(Me)CH	Oil*[3]	77
20	O	CH_3	3-F_3C-C_6H_4	85-88/0.1 mm	80
21	O	CH_3	4-F_3C-C_6H_4	67-68	60
22	O	CH_3	Ph(Me)CH	Oil*[3]	75
23	S	H	3-F_3C-C_6H_4	34	63
24	S	H	4-F_3C-C_6H_4	94-95	80
25[*4]	S	H	Ph(Me)CH	52-53	59
26	S	CH_3	3-F_3C-C_6H_4	91-92	89
27	S	CH_3	4-F_3C-C_6H_4	111-112	88
28	S	CH_3	Ph(Me)CH	Oil*[3]	71

* All compounds are yellow or light yellow.
*[2] Yield of isolated product.
*[3] Purity of compounds 97.5-99.7% (GLC).
*[4] Mp 50-52°C [10].

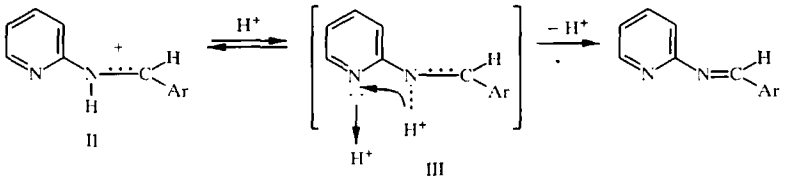
TABLE 3. Elemental Analysis of Solid Imines

Imine	Empirical formula	Found, % / Calculated, %			
		C	H	N	S
1	$C_{10}H_8N_2O$	69.79 / 69.76	4.72 / 4.68	16.24 / 16.27	—
3	$C_{11}H_{10}N_2O$	70.94 / 70.95	5.42 / 5.41	15.10 / 15.04	—
7	$C_{12}H_{12}N_2O$	71.92 / 71.98	6.05 / 6.04	14.04 / 13.99	—
8	$C_{12}H_{12}N_2O$	71.41 / 71.98	5.99 / 6.04	14.07 / 13.99	—
9	$C_{10}H_8N_2S$	63.79 / 63.80	4.18 / 4.28	14.87 / 14.88	17.05 / 17.03
11	$C_{11}H_{10}N_2S$	65.17 / 65.32	4.91 / 4.98	13.98 / 13.85	15.84 / 15.85
12	$C_{11}H_{10}N_2S$	65.28 / 65.32	4.97 / 4.98	13.72 / 13.85	15.88 / 15.85
13	$C_{11}H_{10}N_2S$	64.61 / 65.32	4.87 / 4.98	13.48 / 13.85	15.49 / 15.85
14	$C_{12}H_{12}N_2S$	65.85 / 66.63	5.50 / 5.59	12.46 / 12.95	14.69 / 14.82
15	$C_{12}H_{12}N_2S$	66.47 / 66.63	5.57 / 5.59	13.09 / 12.95	14.85 / 14.82
16	$C_{12}H_{12}N_2S$	66.63 / 66.63	5.54 / 5.59	12.93 / 12.95	14.81 / 14.82
18	$C_{12}H_8F_3NO$	60.22 / 60.26	3.37 / 3.37	5.76 / 5.86	—
21	$C_{13}H_{10}F_3NO$	61.35 / 61.66	4.04 / 3.98	5.47 / 5.53	—
23	$C_{12}H_8F_3NS$	56.43 / 56.46	3.12 / 3.16	5.45 / 5.49	12.56 / 12.56
24	$C_{12}H_8F_3NS$	56.44 / 56.46	3.03 / 3.16	5.45 / 5.49	12.55 / 12.56
25	$C_{13}H_{13}NS$	72.56 / 72.52	5.98 / 6.04	6.48 / 6.50	14.81 / 14.89
26	$C_{13}H_{10}F_3NS$	57.97 / 57.98	3.80 / 3.74	5.16 / 5.20	11.90 / 11.90
27	$C_{13}H_{10}F_3NS$	57.99 / 57.98	3.73 / 3.74	5.17 / 5.20	11.88 / 11.90

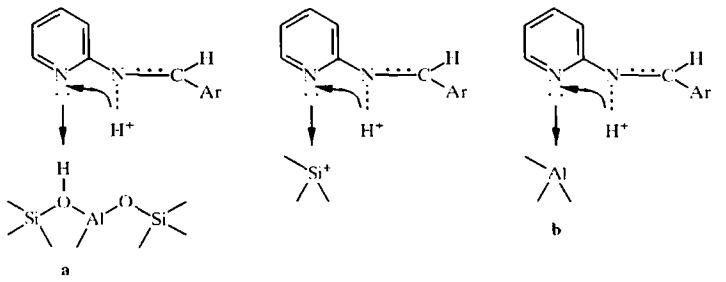
Thus, a simple and convenient method has been developed for the synthesis of the desired imines, most of which were obtained for the first time. The high yields of 2-pyridylazomethines up to 96% (Table 1) indicate the lack of formation of aminals, due apparently to the catalytic action of the molecular sieves. Brönsted and Lewis acid sites are found on the surface of molecular sieves and may form σ-complexes with pyridine compounds (through the ring nitrogen), which enhances the lability of the proton in the amino group, facilitates its elimination, and, thereby, formation of the corresponding imines.

A carbonium–immonium ion is the intermediate species in the condensation of aromatic aldehydes with amines. In the case of reactions with 2-aminopyridines, this ion has structure **II**. A possible mechanism for its conversion to an azomethine through complex **III** is proposed in Scheme 2, while the proposed intermediates formed with the participation of the active sites on the zeolite surface are shown in Scheme 3.

Scheme 2



Scheme 3



Proposed structures of intermediate surface complexes formed in the synthesis of 2-pyridylazomethines in the presence of molecular sieves: *a*) on Bronsted acid sites and *b*) on Lewis acid sites

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Varian Mercury spectrometer at 200 MHz for solutions in $CDCl_3$ with TMS as the internal standard. A modification of the LAOCOON program installed in the spectrometer was used for iteration of the spectra. The mass spectra were taken on an MS-50 mass spectrometer at 70 eV and an HP 6890 GC/MS equipped with a 30.0 m × 250 μm × 0.25 μm HP-5 MS capillary column with temperature programming from 70 to 260°C (10°C/min). The reaction mixtures were analyzed on a Chrom-4 chromatograph equipped with a flame ionization detector and 1.2 m × 3 mm column packed with 5% OV-17 on Chromosorb W-AW (60-80 mesh). The column temperature was 120-250°C and the nitrogen gas carrier flow rate was 60 ml/min.

Benzene was distilled over CaH_2 prior to use. A sample of 5-methyl-2-thiophenecarbaldehyde was prepared according to Campaigne and Archer [13]. The other reagents used in this work were obtained from Fluka, Merck, and Acros. The aldehydes and 3-trifluoromethylaniline were purified by vacuum distillation, while 2-aminopyridine was recrystallized from benzene. The characteristics of these samples corresponded to literature data. The other substrates were used without purification. VEB Laborchemie Apolda 4A molecular sieves were used.

General Method for the Synthesis of Azomethines 1-28. A sample of dry benzene (10 ml) was introduced into a flask. Then, starting aldehyde (5 mmol) and amine (5 mmol) were added followed by freshly roasted molecular sieves (5 g). The mixture was maintained at room temperature, periodically taking samples and analyzing them by gas–liquid chromatography and GC/MS. After some time depending on the substrate (Table 1), the starting reagents were almost completely converted to the corresponding products. At the end of the reaction, the sieves were filtered off and washed with benzene. The filtrate was evaporated at 40°C (15 mm) and the traces of the starting compounds were removed at 45-50°C (0.1 mm). The products, which are either oils or light yellow or white crystalline compounds, were purified by vacuum distillation or recrystallization from petroleum ether, benzene, or their mixture. The characteristics of these products were then determined (Tables 1-3) and the ^{1}H NMR spectra were taken.

2-Amino-N-(2-furylmethyliden)pyridine (1). Mass spectrum, *m/z* (I_{rel}, %): 172 (29, M^+), 171 (19, $[M - H]^+$), 144 (40, $[M - CO]^+$), 143 (19, $[M - HCO]^+$), 131 (6), 119 (10), 118 (100, $[C_5H_4NNCHCH]^+$), 117 (9), 105 (2), 95 (2, $[M - Fur]^+$), 79 (55, $[PyH]^+$), 78 (33, Py^+), 64 (6), 52 (39), 51 (41), 39 (25). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 6.57 (1H, dd, *J* = 3.4 and 1.6, FurH-4); 7.05 (1H, d, *J* = 3.4, FurH-3); 7.15 (1H, m, *J* = 7.6 and 4.8, PyH-5); 7.40 (1H, d, *J* = 7.6, PyH-3); 7.64 (1H, m, *J* = 1.6, FurH-5); 7.73 (1H, td, *J* = 7.6 and 1.8, PyH-4); 8.45 (1H, dd, *J* = 4.8 and 1.8, PyH-6); 9.10 (1H, s, CH=N).

2-Amino-N-(2-furylmethyliden)-3-methylpyridine (2). Mass spectrum, *m/z* (I_{rel}, %): 186 (38, M^+), 185 (26, $[M - H]^+$), 171 (1, $[M - Me]^+$), 158 (24, $[M - CO]^+$), 157 (28, $[M - HCO]^+$), 145 (5), 133 (10), 132 (100, $[MeC_5H_3NNCHCH]^+$), 131 (14), 119 (2, $[M - Fur]^+$), 93 (45, $[MeC_5H_3N - H]^+$), 92 (23, $[MeC_5H_3N]^+$), 78 (8, Py^+), 66 (20), 65 (36), 64 (9), 52 (19), 51 (23), 39 (46). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.47 (3H, s, CH_3); 6.56 (1H, dd, *J* = 3.5 and 1.7, FurH-4); 7.03 (1H, d, *J* = 3.5, FurH-3); 7.07 (1H, dd, *J* = 7.4 and 4.7, PyH-5); 7.53 (1H, d, *J* = 7.4, PyH-4); 7.64 (1H, d, *J* = 1.7, FurH-5); 8.27 (1H, dd, *J* = 4.7 and 1.6, PyH-6); 8.94 (1H, s, CH=N).

2-Amino-N-(2-furylmethyliden)-4-methylpyridine (3). Mass spectrum, *m/z* (I_{rel}, %): 186 (23, M^+), 185 (12, $[M - H]^+$), 158 (25, $[M - CO]^+$), 157 (10, $[M - HCO]^+$), 145 (5), 133 (10), 132 (100, $[MeC_5H_3NNCHCH]^+$), 131 (11), 106 (2), 93 (35, $[MeC_5H_3N - H]^+$), 92 (15, $[MeC_5H_3N]^+$), 78 (6, Py^+), 66 (19), 65 (20), 64 (6), 52 (11), 51 (16), 39 (26). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.37 (3H, s, CH_3); 6.56 (1H, dd, *J* = 3.4 and 1.2, FurH-4); 6.99 (1h, br. d, *J* = 5.0, PyH-5); 7.03 (1H, d, *J* = 3.4, FurH-3); 7.24 (1H, s, PyH-3); 7.64 (1H, d, *J* = 1.2, FurH-5); 8.30 (1H, d, *J* = 5.0, PyH-6); 9.09 (1H, s, CH=N).

2-Amino-N-(2-furylmethyliden)-6-methylpyridine (4). Mass spectrum, *m/z* (I_{rel}, %): 186 (37, M^+), 185 (28, $[M - H]^+$), 171 (2, $[M - Me]^+$) 169 (4), 158 (33, $[M - CO]^+$), 157 (33, $[M - HCO]^+$), 156 (11), 155 (12), 143 (9), 133 (8), 132 (65, $[MeC_5H_3NNCHCH]^+$), 131 (9), 93 (100, $[MeC_5H_3NH]^+$), 92 (22, $[MeC_5H_3N]^+$), 78 (9, Py^+), 66 (42), 65 (43), 64 (11), 52 (20), 51 (23), 39 (51). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.53 (3H, s, CH_3); 6.55 (1H, dd, *J* = 3.4 and 1.6, FurH-4); 7.01 (1H, d, *J* = 7.6, PyH-5); 7.03 (1H, d, *J* = 3.4, FurH-3); 7.19 (1H, d, *J* = 7.6, PyH-3); 7.60 (1H, t, *J* = 7.6, PyH-4); 7.62 (1H, d, *J* = 1.6, FurH-5); 9.09 (1H, s, CH=N).

2-Amino-N-(5-methyl-2-furylmethyliden)pyridine (5). Mass spectrum, *m/z* (I_{rel}, %): 186 (46, M^+), 172 (13), 171 (100, $[M - Me]^+$), 157 (2, $[M - HCO]^+$), 143 (17, $[M - MeCO]^+$), 142 (6), 116 (14), 89 (4), 79 (56, $[PyH]^+$), 78 (27, Py^+), 65 (4), 64 (11), 52 (23), 51 (30), 43 (12), 39 (10). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.43 (3H, s, CH_3); 6.19 (1H, br. d, J = 3.4, FurH-4); 6.94 (1H, d, *J* = 3.4, FurH-3); 7.13 (1H, ddd, *J* = 7.9, 4.8 and 1.6, PyH-5); 7.40 (1H, d, *J* = 7.9, PyH-3); 7.71 (1H, td, *J* = 7.9 and 1.6, PyH-4); 8.43 (1H, dd, *J* = 4.8 and 1.6, PyH-6); 9.00 (1H, s, CH=N).

2-Amino-3-methyl-N-(5-methyl-2-furylmethyliden)pyridine (6). Mass spectrum, *m/z* (I_{rel}, %): 200 (45, M^+), 186 (13), 185 (100, $[M - Me]^+$), 171 (2), 170 (3, $[M - 2Me]^+$), 157 (18, $[M - MeCO]^+$), 156 (9), 142 (5), 130 (3), 119 (2, $[M - MeC_4H_2O]^+$), 103 (2), 93 (36, $[MeC_5H_3NH]^+$), 92 (17, $[MeC_5H_3N]^+$), 79 (8, PyH^+), 66 (10), 65 (24), 64 (9), 53 (11), 51 (14), 43 (11), 39 (19). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.42 (3H, s, $FurC\underline{H}_3$); 2.45 (3H, s, $PyC\underline{H}_3$); 6.16 (1H, br. d, *J* = 2.8, FurH-4); 6.91 (1H, d, *J* = 2.8, FurH-3); 7.03 (1H, dd, *J* = 7.4 and 4.8, PyH-5); 7.50 (1H, br. d, *J* = 7.4, PyH-4); 8.25 (1H, dd, *J* = 4.8 and 1.6, PyH-6); 8.81 (1H, s, CH=N).

2-Amino-4-methyl-N-(5-methyl-2-furylmethyliden)pyridine (7). Mass spectrum, *m/z* (I_{rel}, %): 200 (48, M^+), 199 (8, $[M - H]^+$), 186 (14), 185, $[M - Me]^+$), 171 (2), 170 (6, $[M - 2Me]^+$), 157 (14, $[M - MeCO]^+$), 156 (9), 142 (6), 132 (3), 130 (4), 93 (56, $[MeC_5H_3NH]^+$), 92 (16 $[MeC_5H_3N]^+$), 79 (9, $[PyH]^+$), 66 (18), 65 (25), 64 (6),

53 (13), 51 (14), 43 (13), 39 (18). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.36 (3H, s, FurC<u>H</u>$_3$); 2.44 (3H, s, PyC<u>H</u>$_3$); 6.19 (1H, br. d, *J* = 3.4, FurH-4); 6.93 (1H, d, *J* = 3.4, FurH-3); 6.96 (1H, br. d, *J* = 5.2, PyH-5); 7.23 (1H, br. s, PyH-3); 8.29 (1H, d, *J* = 5.2, PyH-6); 9.00 (1H, s, CH=N).

2-Amino-6-methyl-N-(5-methyl-2-furylmethyliden)pyridine (8). Mass spectrum, *m/z* (I_{rel}, %): 200 (30, M^+), 185 (29, $[M - Me]^+$), 170 (3, $[M - 2Me]^+$), 157 (58, $[M - MeCO]^+$), 156 (29), 155 (18), 143 (7), 130 (3), 120 (2), 93 (100, $[MeC_5H_3NH]^+$), 92 (18, $[MeC_5H_3N]^+$), 79 (10, $[PyH]^+$), 66 (28), 65 (35), 64 (9), 53 (13), 51 (18), 43 (17), 39 (28). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.41 (3H, s, FurC<u>H</u>$_3$); 2.52 (3H, s, PyC<u>H</u>$_3$); 6.16 (1H, br. d, *J* = 3.2, FurH-4); 6.92 (1H, d, FurH-3); 6.97 (1H, d, *J* = 7.6, PyH-5); 7.18 (1H, d, *J* = 7.6, PyH-4); 8.99 (1H, s, CH=N).

2-Amino-N-(2-thienylmethyliden)pyridine (9). Mass spectrum, *m/z* (I_{rel}, %): 188 (22, M^+), 187 (20, $[M - H]^+$), 160 (2), 155 (3), 134 (1), 110 (2, $[M - Py]^+$), 109 (3), 117 (9), 105 (2), 95 (3), 85 (2, $[M - Th]^+$), 79 (100, $[PyH]^+$), 78 (18, Py^+), 70 (5), 64 (2), 58 (3), 52 (24), 51 (20), 39 (14). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 7.15 (2H, m, PyH-5, ThH-4); 7.32 (1H, d, *J* = 8.2, PyH-3); 7.5-7.6 (2H, m, ThH-3,5); 7.72 (1H, d.t, *J* = 7.8 and 1.8, PyH-4); 8.46 (1H, dd, *J* = 4,8 and 1.8, PyH-6); 9.33 (1H, s, CH=N).

2-Amino-3-methyl-N-(2-thienylmethyliden)pyridine (10). Mass spectrum, *m/z* (I_{rel}, %): 202 (24, M^+), 201 (23, $[M - H]^+$), 187 (2, $[M - Me]^+$), 169 (18), 157 (2), 110 (3), 93 (100, $[MeC_5H_3H - H]^+$), 92 (13, $[MeC_5H_3N]^+$), 78 (4, Py^+), 66 (22), 65 (18), 52 (7), 51 (6), 45 (7), 39 (19). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.43 (3H, s, CH_3); 7.05 (1H, dd, *J* = 7.6 and 4.6, PyH-5); 7.11 (1H, dd, *J* = 4.8 and 3.6, ThH-4, PyH-3); 7.5-7.6 (3H, m, PyH-4, ThH-3,5); 8.26 (1H, dd, *J* = 4.6 and 1.8, PyH-6); 9.21 (1H, s, CH=N).

2-Amino-4-methyl-N-(2-thienylmethyliden)pyridine (11). Mass spectrum, *m/z* (I_{rel}, %): 202 (17, M^+), 201 (19, $[M - H]^+$), 187 (2, $[M - Me]^+$), 169 (2), 157 (2), 110 (3), 109 (3), 93 (100, $[MeC_5H_3N - H]^+$), 92 (13, $[MeC_5H_3N]^+$), 78 (4, Py^+), 66 (22), 65 (18), 52 (7), 51 (6), 45 (7), 39 (19). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.37 (3H, s, CH_3); 6.98 (1H, br. d, *J* = 5.0, PyH-5); 7.1-7.2 (2H, m, ThH-4, PyH-3); 7.5-7.6 (2H, m, ThH-3,5); 8.31 (1H, d, *J* = 5.0, PyH-6); 9.33 (1H, s, CH=N).

2-Amino-6-methyl-N-(2-thienylmethyliden)pyridine (12). Mass spectrum, *m/z* (I_{rel}, %): 202 (16, M^+), 169 (2), 155 (2), 110 (3), 93 (100, $[MeC_5H_3N - H]^+$), 92 (10, $[MeC_5H_3N]^+$), 78 (4, Py^+), 66 (20), 65 (16), 51 (5), 45 (6), 39 (16). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.53 (3H, s, CH_3); 6.92-7.22 (3H, m, PyH-3,5, ThH-4); 7.4-7.7 (2H, m, PyH-4, ThH-3,5); 9.27 (1H, s, CH=N).

2-Amino-N-(5-methyl-2-thienylmethyliden)pyridine (13). Mass spectrum, *m/z* (I_{rel}, %): 202 (26, M^+), 201 (21, $[M - H]^+$), 187 (3, $[M - Me]^+$), 175 (2), 169 (7), 155 (2), 142 (6), 122 (5), 109 (2), 97 (6), 79 (100, $[Py]^+$), 78 (19, Py^+), 69 (5), 52 (20), 51 (15), 45 (7), 39 (8). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.54 (3H, br. s, CH_3); 6.81 (1H, br. d, *J* = 4.2, ThH-4); 7.12 (1H, ddd, *J* = 7.6, 4.8 and 1.2, PyH-5); 7.29 (1H, d, *J* = 8.2, PyH-3); 7.39 (1H, d, *J* = 4.2, ThH-3); 7.70 (1H, dt, *J* = 7.6 and 1.8, PyH-4); 8.44 (1H, dd, *J* = 4.8 and 1.8, PyH-6); 9.22 (1H, s, CH=N).

2-Amino-3-methyl-N-(5-methyl-2-thienylmethyliden)pyridine (14). Mass spectrum, *m/z* (I_{rel}, %): 216 (20, M^+), 215 (16, $[M - H]^+$), 201 (5, $[M - Me]^+$), 189 (1), 183 (14), 168 (3), 93 (100, $MeC_5H_3N - H]^+$), 92 (17, $[MeC_5H_3N]^+$), 78 (3, Py^+), 66 (15), 65 (19), 53 (8), 51 (7), 45 (7), 39 (17). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.41 (3H, s, PyC<u>H</u>$_3$); 2.53 (3H, s, ThC<u>H</u>$_3$); 6.78 (1H, br. d, *J* = 3.6, ThH-4); 7.03 (1H, m, PyH-5); 7.35 (1H, d, *J* = 3.6, ThH-3); 7.49 (1H, br. d, *J* = 7.0, PyH-4); 8.25 (1H, br. d, *J* = 4.6, PyH-6); 9.10 (1H, s, CH=N).

2-Amino-4-methyl-N-(5-methyl-2-thienylmethyliden)pyridine (15). Mass spectrum, *m/z* (I_{rel}, %): 216 (15, M^+), 215 (13, $[M - H]^+$), 201 (2, $[M - Me]^+$), 189 (1), 183 (2), 168 (1), 93 (100, $[MeC_5H_3N - H]^+$), 92 (10, $[MeC_5H_3N]^+$), 78 (2, Py^+), 66 (18), 65 (16), 53 (7), 51 (5), 45 (5), 39 (12). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.35 (3H, s, PyC<u>H</u>$_3$); 2.54 (3H, s, ThC<u>H</u>$_3$); 6.79 (1H, br. d, *J* = 3.6, ThH-4); 6.95 (1H, br. d, *J* = 5.0, PyH-5); 7.12 (1H, br. s, PyH-3); 7.37 (1H, d, *J* = 3.6, ThH-3); 8.29 (1H, d, *J* = 5.0, PyH-6); 9.10 (1H, s, CH=N).

2-Amino-6-methyl-N-(5-methyl-2-thienylmethyliden)pyridine (16). Mass spectrum, *m/z* (I_{rel}, %): 216 (21, M^+), 215 (3, $[M - H]^+$), 201 (2, $[M - Me]^+$), 122 (3), 109 (2), 97 (5), 93 (100, $[MeC_5H_3N - H]^+$), 92 (9, $[MeC_5H_3N]^+$), 78 (4, Py^+), 66 (20), 65 (16), 53 (6), 51 (5), 45 (5), 39 (12). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.54 (6H, s, $2CH_3$); 6.79 (1H, br. d, *J* = 3.6, ThH-4); 6.98 (1H, d, *J* = 7.8, PyH-5); 7.06 (1H, d, *J* = 7.6, PyH-3); 7.37 (1H, d, *J* = 3.6, ThH-3); 7.58 (1H, dd, *J* = 7.8 and 7.6, PyH-4); 9.16 (1H, s, CH=N).

N-(2-Furylmethylidene)-3-trifluoromethylaniline (17). Mass spectrum, *m/z* (I_{rel}, %): 240 (19, $[M + H]^+$), 239 (100, M^+), 238 (61, $[M - H]^+$), 220 (10, $[M - F]^+$), 211 (18), 210 (23, $[M - HCO]^+$), 185 (11), 172 (8, $[M - Fur]^+$), 170 (9, $[M - CF_3]^+$), 145 (62 $[C_6H_4CF_3]^+$), 125 (11), 95 (15), 75 (14), 69 (7), 68 (7, $FurH^+$), 51 (11), 39 (19). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 6.51 (1H, dd, *J* = 5 and 2, FurH-4); 6.91 (1H, d, *J* = FurH-3); 7.2-7.5 (4H, m, Ar); 7.58 (1H, m, *J* = 2, FurH-5); 8.24 (1H, s, CH=N).

N-(2-Furylmethylidene)-4-trifluoromethylaniline (18). Mass spectrum, *m/z* (I_{rel}, %): 240 (13, $[M + H]^+$), 239 (100, M^+), 238 (55, $[M - H]^+$), 220 (17, $[M - F]^+$), 211 (25), 210 (37, $[M - HCO]^+$), 185 (13), 172 (6, $[M - Fur]^+$), 170 (11, $[M - CF_3]^+$), 145 (56 $[C_6H_4CF_3]^+$), 125 (12), 115 (11), 95 (17), 75 (18), 68 (6. $FurH^+$), 50 (10), 39 (15), 32 (9). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 6.63 (1H, dd, *J* = 4 and 3.6, FurH-4); 7.04 (1H, d, *J* = 4, FurH-3); 7.33 (2H, d, *J* = 8, ArH-3,5); 7.64 (2H, d, *J* = 8, ArH-2,6); 7.67 (1H, m, J_1 = 3.6, FurH-5); 8.29 (1H, s, CH=N).

N-(2-Furylmethylidene)-1-phenylethylamine (19). Mass spectrum, *m/z* (I_{rel}, %): 199 (34, M^+), 184 (22, $[M - Me]^+$), 105 (100, $[Ph(Me)HC]^+$), 103 (11), 79 (16), 77 (23, Ph^+), 51 (16), 39 (14). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 1.55 (3H, d, *J* = 7, CH_3); 4.44 (1H, q, *J* = 5, CHN); 6.42 (1H, dd, *J* = 5 and 2, FurH-4); 6.69 (1H, d, *J* = 5, FurH-3); 7.1-7.4 (5H, m, Ph); 7.47 (1H, d, *J* = 2, FurH-5); 8.10 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-3-trifluoromethylaniline (20). Mass spectrum, *m/z* (I_{rel}, %): 254 (15, $[M + H]^+$), 253 (100, M^+), 252 (42, $[M - H]^+$), 238 (25, $[M - Me]^+$), 234 (9, $[M - F]^+$), 218 (14), 211 (19), 210 (29, $[M - MeCO]^+$), 190 (12), 185 (10), 183 (13), 172 (12), 145 (67, $[C_6H_4CF_3]^+$), 125 (13), 95 (21), 81 (15), 75 (18), 69 (9), 53 (37), 43 (63), 39 (24). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.40 (3H, d, *J* = 0.9, CH_3); 6.15 (1H, dq, *J* = 4 and 0.9, FurH-4); 6.84 (1H, d, *J* = 4, FurH-3); 7.2-7.5 (4H, m, Ar); 8.12 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-4-trifluoromethylpyridine (21). Mass spectrum, *m/z* (I_{rel}, %): 254 (15, $[M + H]^+$), 253 (100, M^+), 252 (35, $[M - H]^+$), 238 (24, $[M - Me]^+$), 234 (16, $[M - F]^+$), 218 (5), 211 (26), 210 (37, $[M - MeCO]^+$), 190 (8), 185 (11), 183 (14), 172 (6), 145 (50, $[C_6H_4CF_3]^+$), 125 (12), 95 (15), 82 (10), 75 (13), 69 (6), 53 (18), 51 (14), 43 (27), 39 (9). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.44 (3H, d, *J* = 0.9, CH_3); 6.18 (1H, dq, *J* = 4 and 0.9, FurH-4); 6.89 (1H, d, *J* = 4, FurH-3); 7.24 (2H, d, *J* = 8, ArH-3,5); 7.60 (2H, d, *J* = 8, ArH-2,6); 8.13 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-1-phenylethylamine (22). Mass spectrum, *m/z* (I_{rel}, %): 213 (36, M^+), 198 (41, $[M - Me]^+$), 136 (5, $[M - Ph]^+$), 105 (100, $[Ph(Me)HC]^+$), 103 (13), 79 (27), 77 (25, Ph^+), 51 (18), 43 (14), 39 (8). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 1.60 (3H, d, *J* = 7, CH_3CH); 2.34 (3H, d, *J* = 1, CH_3-Fur); 4.45 (1H, q, *J* = 7, CH-N); 6.02 (1H, dq, *J* = 4 and 1, FurH-4); 6.58 (1H, d, *J* = 4, FurH-3); 7.1-7.4 (5H, m, Ph); 8.00 (1H, s, CH=N).

N-(2-Thienylmethylidene)-3-trifluoromethylaniline (23). Mass spectrum, *m/z* (I_{rel}, %): 256 (16, $[M + H]^+$), 255 (86, M^+), 254 (100, $[M - H]^+$), 236 (6, $[M - F]^+$), 186 (5, $[M - CF_3]^+$), 172 (5), 145 (59, $[C_6H_4CF_3]^+$), 125 (10), 95 (21), 84 (10, $[ThH]^+$), 75 (14), 69 (12), 51 (10), 45 (12), 39 (16). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 7.11 (1H, dd, *J* = 5 and 4, ThH-4); 7.2-7.6 (6H, m, Ar, ThH-3,5); 8.55 (1H, s, CH=N).

N-(2-Thienylmethylidene)-4-trifluoromethylaniline (24). Mass spectrum, *m/z* (I_{rel}, %): 256 (17, $[M + H]^+$), 255 (85, M^+), 254 (100, $[M - H]^+$), 236 (11, $[M - F]^+$), 186 (7, $[M - CF_3]^+$), 172 (4), 145 (40, $[C_6H_4CF_3]^+$), 125 (9), 95 (15), 84 (5, $[ThH]^+$), 75 (10), 69 (8), 51 (6), 45 (7), 39 (8). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 7.11 (1H, dd, *J* = 6 and 4.6, ThH-4); 7.22 (1H, d, *J* = 9, ArH-3,5); 7.53 (2H, m, *J* = 6 and 4.6, ThH-3,5); 7.62 (1H, d, *J* = 9, ArH-2,6); 8.55 (1H, s, CH=N).

1-Phenylethyl-N-(2-thienylmethylidene)amine (25). Mass spectrum, *m/z* (I_{rel}, %): 215 (31, M^+), 200 (22, $[M - Me]^+$), 105 (100, $[Ph(Me)HC]^+$), 103 (11), 96 (10), 79 (15), 77 (23, Ph^+), 51 (11), 39 (14). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 1.53 (3H, d, *J* = 7, CH_3); 4.47 (1H, q, *J* = 7, CH–N); 7.00 (1H, dd, *J* = 5 and 4, ThH-4); 7.0-7.5 (7H, m, Ph, ThH-3,5); 8.38 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-3-trifluoromethylaniline (26). Mass spectrum, *m/z* (I_{rel}, %): 270 (16, $[M + H]^+$), 269 (86, M^+), 268 (100, $[M - H]^+$), 250 (9, $[M - F]^+$), 235 (3, $[M - Me - F]^+$), 200 (5, $[M - CF_3]^+$), 172 (5), 145 (38, $[C_6H_4CF_3]^+$), 125 (10), 97 (26, $[MeTh]^+$), 95 (17), 77 (10), 69 (11), 53 (10), 45 (10), 37 (7). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.40 (3H, d, *J* = 1, CH_3); 6.15 (1H, dq, *J* = 4 and 1, ThH-4); 6.84 (1H, d, *J* = 4, ThH-3); 7.2-7.5 (4H, m, Ar); 8.12 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-4-trifluoromethylaniline (27). Mass spectrum, *m/z* (I_{rel}, %): 270 (18, $[M + H]^+$), 269 (82, M^+), 268 (100, $[M - H]^+$), 250 (9, $[M - F]^+$), 200 (8, $[M - CF_3]^+$), 172 (5), 145 (32, $[C_6H_4CF_3]^+$), 125 (10), 97 (15, $[MeTh]^+$), 95 (14), 77 (6), 69 (9, CF_3), 53 (5), 45 (5), 37 (4). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 2.55 (3H, d, *J* = 1, CH_3); 6.80 (1H, dq, *J* = 4 and 1, ThH-4); 7.21 (1H, d, *J* = 8, ArH-3,5); 7.33 (1H, d, *J* = 4, ThH-3); 7.60 (1H, d, *J* = 8, ArH-2,6); 8.41 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-1-phenylethylamine (28). Mass spectrum, *m/z* (I_{rel}, %): 229 (33, M^+), 214 (36, $[M - Me]^+$), 152 (5, $[M - Ph]^+$), 105 (100, $[Ph(Me)HC]^+$), 103 (12), 97 (5, $[MeTh]^+$), 79 (16), 77 (26, Ph^+), 51 (12), 45 (7), 39 (8). ^{1}H NMR spectrum, δ (ppm), *J* (Hz): 1.51 (3H, d, *J* = 7, CH_3CH); 2.47 (3H, d, *J* = 0.9, CH_3Th); 4.42 (1H, q, *J* = 7, CH-N); 6.64 (1H, dq, *J* = 5 and 0.9, ThH-4); 7.02 (1H, d, *J* = ThH-3); 7.1-7.4 (5H, m, Ph); 8.27 (1H, s, CH=N).

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