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REACTIONS OF 5-[3-(TRIFLUOROMETHYL)-PHENYL]FURAN-2-CARBALDEHYDE

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The Knoevenagel condensations of 5-[3-(trifluoromethyl)phenyl]furan-2-carbaldehyde with seven compounds containing an active methyl or methylene group have been studied. The compounds used were: methyl 2-cyanoacetate, malononitrile, 2-furylacetonitrile, acetophenone, 2-thioxo-1,3-thiazolidin-4-one (rhodanine), 5,5-dimethylcyclohexane-1,3-dione (dimedone), and methyl 2-azidoacetate. The effect of microwave irradiation on the condensation reactions was studied and compared with "classical" conditions. Thermolysis of methyl 2-azido-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}propenoate afforded methyl 2-[3-(trifluoromethyl)phenyl)]-4H-furo[3,2-b]pyrrole-5-carboxylate. (2E)-3-{5-[3-(Trifluoromethyl)phenyl]-2-furyl}propenoic acid was converted to the corresponding azide, which was cyclized on heating into 2-[3-(trifluoromethyl)phenyl)]-4,5-dihydrofuro[3,2-c]pyridin-4-one. The latter after successive action of $POCl_3$ and NH_2NH_2–Pd/C gave 2-[3-(trifluoromethyl)-phenyl]furo[3,2-c]pyridine.

Keywords: methyl 2-[3-(trifluoromethyl)phenyl)]-4H-furo[3,2-*b*]pyrrole-5-carboxylate, 5-[3-(trifluoromethyl)phenyl]furan-2-carbaldehyde, 2-[3-(trifluoromethyl)phenyl)]furo[3,2-*c*]pyridine, Knoevenagel reaction.

During the past few decades many results have been published in the field of synthesis and study of physical and chemical properties of heterocyclic compounds containing a furan ring connected or fused with a benzene ring or with different heterocyclic systems.

Substituted furans are ubiquitous structural units in natural products and pharmaceuticals [1] and have been widely used as synthetic intermediates [2, 3]. Many of the published condensation products are biologically active compounds [4, 5] or can be used as intermediates in organic synthesis [6-9].

In the past two decades one of us was interested in the syntheses, reaction, and aromaticity of variously substituted furo[3,2-*b*]pyrroles and their [2,3-*b*]-isomers [10, 11]. Substitution, addition, and cycloaddition reactions of furo[3,2-*b*]pyrroles and their condensed derivatives involving the interesting transformations of furo[3,2-*b*]pyrrole system were presented. We also reported on the synthesis of 2-arylfuro[3,2-*c*]pyridines [12, 13] and 2,3-dimethylfuro[3,2-*c*]pyridine [14]. Later on some furo[3,2-*c*]pyridines have been used for the preparation of Cu(II) and Ni(II) complexes [15]. Furo[3,2-*c*]pyridine and its 2-methyl-, 2,3-dimethyl- and benzo[4,5] derivative were used for the first time as ligands to synthesize potentially new Werner clathrates, and the structural characterization, spectral, and magnetic properties of isothiocyanate nickel(II) complexes were published [16, 17].

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The aim of this paper is to use 5-[3-(trifluoromethyl)phenyl]furan-2-carbaldehyde (**1**) in the synthesis of fused aromatic heterocyclic systems containing the furan ring fused with pyrrole or pyridine rings. First of all some new condensation products of the title aldehyde with active methyl and methylene compounds were synthesized (Scheme 1). The reactions of aldehyde **1** with methyl 2-cyanoacetate resulted in methyl (2*E*)-2-cyano-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}propenoate (**2**), with malono- nitrile in {5-[3-(trifluoromethyl)phenyl]-2-furyl}methylenemalononitrile (**3**), with 2-furylacetonitrile in (2*E*)-2-(2-furyl)-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}acrylonitrile (**4**), with acetophenone in (2*E*)-1-phenyl-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}prop-2-en-1-one (**5**), with 2-thioxo-1,3-thiazolidin-4-one in 2-thioxo-5-{5-[3-(trifluoromethyl)phenyl]-2-furyl}methylene-1,3-thiazolidin-4-one (**6**), and with 5,5-dimethylcyclohexane-1,3-dione in 2-{5-[3-(trifluoromethyl)phenyl]-2-furyl}methylene-5,5-dimethylcyclohexane-1,3-dione (**7**). The mentioned compounds were prepared in Knoevenagel conditions; sodium methoxide or hydroxide, potassium acetate, or piperidine were used as basic catalysts. All the condensation products are quite high-melting stable yellow-orange solids that are sparingly soluble in common solvents. Yields of these reactions are comparable with those published in our previous papers on the condensation of 5-arylfuran-2-carbaldehydes with the same active methylene compounds [18, 19].

The effect of microwave irradiation on the condensation reactions was studied and compared with "classical" conditions (Table 1). The results showed that microwave irradiation shortens the reaction time while affording comparable or an improved yield of compound **5**.

The configuration assignment of the substituents on the double bond for compound **2** has been determined by ^{13}C NMR spectra using the stereospecific coupling constant $^{3}J_{CN,H\text{-}7}$ = 13.76 Hz, which confirms that it is the *E*-isomer [20]. Analogously with our previous paper [21], compound **4** is an *E*-isomer as well.

Compound **5** belongs to α,β-unsaturated ketones (chalcones), which were in the past the subject of our study [22]. The ^{1}H NMR spectrum of compound **5** displays doublets for double bond protons at 7.61 ppm for H-12 and 7.52 ppm for H-13. The coupling constant of protons H-12 and H-13 is 15.5 Hz, which shows the *E*-configuration of the double bond.

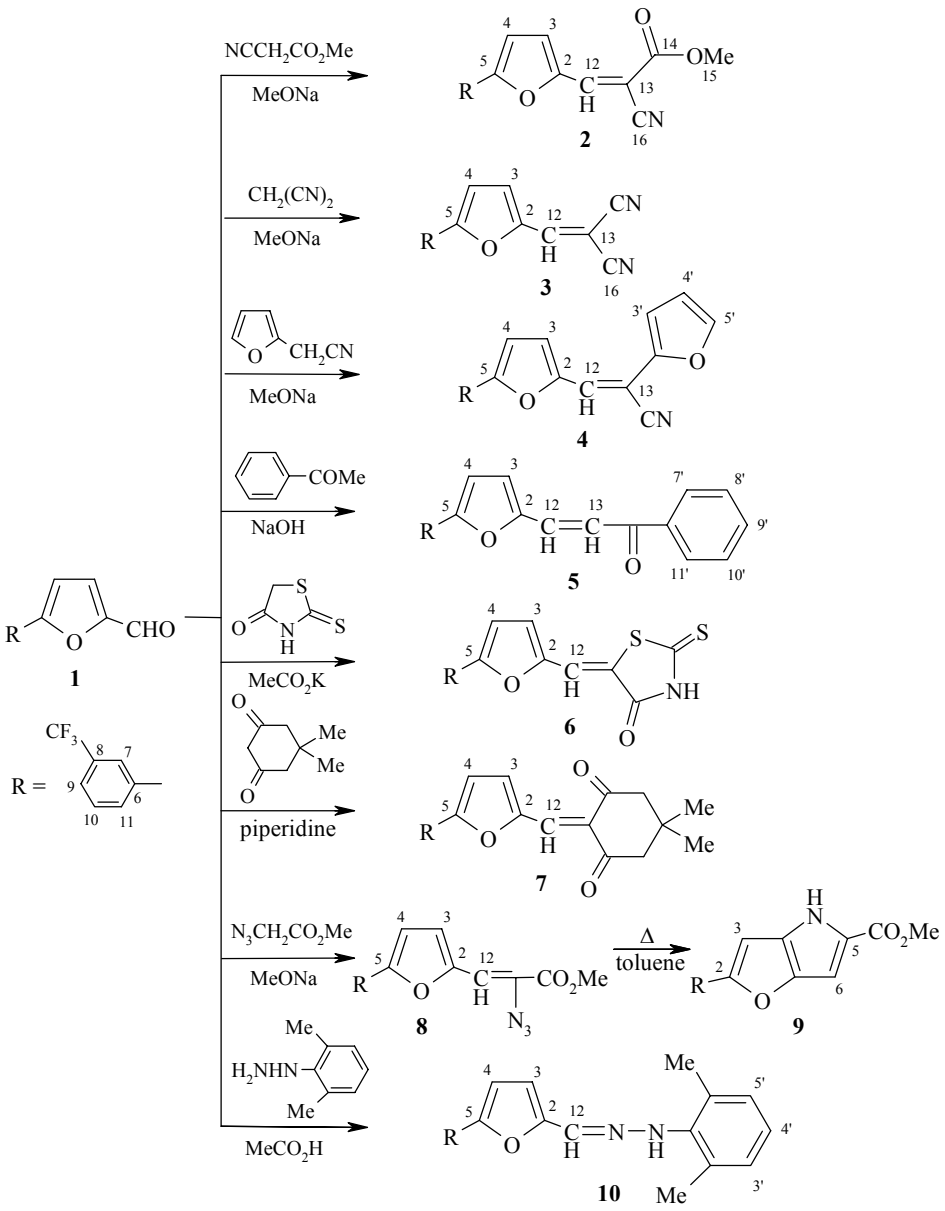
The reaction of aldehyde **1** with methyl azidoacetate in the presence of sodium methoxide was found to proceed smoothly to give azide **8**, the thermolysis of which was carried out in boiling toluene leading to methyl 2-[3-(trifluoromethyl)phenyl]-4H-furo[3,2-*b*]pyrrole-5-carboxylate (**9**). The thermolysis of azide **8** proceeds relatively rapidly until the liberation of nitrogen ceased, affording ester **9** in moderate yield (Scheme 1). The preparation of compound **9** has not been published until now, but some of its reactions have been published recently [23].

In our former paper [24] we described the reaction of 5-arylfuran-2-carbaldehydes with 2,6-dialkylphenylhydrazines to give the corresponding hydrazones in excellent yields. Analogously 5-[3-(trifluoromethyl)phenyl]furan-2-carbaldehyde-2,6-dimethylphenylhydrazone (**10**) was obtained in moderate yield starting from aldehyde **1** and 2,6-dimethylphenylhydrazine. The ^{1}H NMR display doublets of H-3 and H-4 protons of the furan ring with coupling constant $J_{3,4}$ = 3.5 Hz and a singlet of H-12.

TABLE 1. Comparison of "Classical" and Microwave-activated Reactions

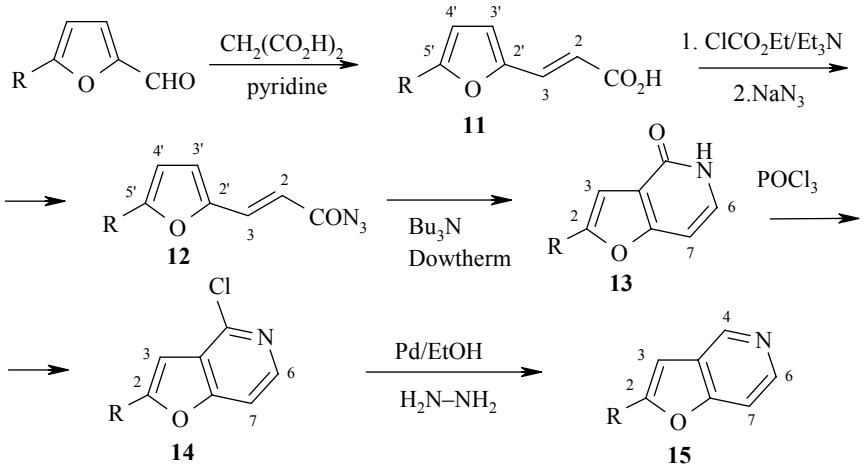
Compound	Classical conditions		MW reaction	
	Reaction time, min	Yield, %	Reaction time, min	Yield, %
2	10	85.3	2	85.4
5	30	48.1	1	81.8
6	30	43.1	2	46

Scheme 1



(2*E*)-3-{5-[3-(Trifluoromethyl)phenyl]-2-furyl}propenoic acid (**11**) was prepared according our previously published procedure [13] and converted to the (2*E*)-3-{5-[3-(trifluormethyl)phenyl]-2-furyl}propenoic azide (**12**), which in turn was cyclized by heating in Dowtherm to give 2-[3-(trifluoromethyl)phenyl]-4,5-dihydrofuro[3,2-*c*]pyridin-4-one (**13**). Pyridone **13** was aromatized with phosphorus oxychloride to 4-chloro-2-[3-(trifluoromethyl)phenyl]furo[3,2-*c*]pyridine (**14**), which was transformed into 2-[3-(trifluoromethyl)phenyl]furo[3,2-*c*]pyridine (**15**) by hydrazine hydrate on Pd/C (Scheme 2).

Scheme 2



R = 3-trifluoromethylphenyl

EXPERIMENTAL

Melting points were determined using a Kofler hot plate apparatus and are uncorrected. All solvents were pre-distilled and dried appropriately prior to use. Concentration and evaporation refer to the removal of volatile materials under reduced pressure using a Buchi Rotovapor. Elemental analyses of compounds **2-15** were determined using a Carlo Erba CHNS-OEA 1108-Elemental Analyzer. UV spectra were measured on a WPA UV-vis Diode-Array spectrophotometer (Cambridge, UK) in methanol and presented as λ_{max} (log ε); λ_{max} values are given in nm, and ε in $m^2 \cdot mol^{-1}$. ^1H and ^{13}C NMR spectra were obtained using a Bruker AMX (360 and 90 MHz, respectively) in DMSO-d_6 with TMS as an internal standard reference. The methods used for the assignment were gs-H,H-COSY, gs-HSQC, and gs-HMBC. Microwave reactions were carried out in a Whirlpool type microwave oven at 90-500 W. The apparatus was adapted for laboratory applications: *n*-hexane was used as coolant for the condenser.

The starting 5-[3-(trifluormethyl)phenyl]furan-2-carbaldehyde (**1**) was prepared according to [25]; 5,5-dimethylcyclohexane-1,3-dione (dimedone) (Aldrich) was used without purification.

Methyl (2*E*)-2-Cyano-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}propenoate (2). Compound **1** (2.4 g, 10 mmol) was dissolved in absolute methanol (40 ml); methyl cyanoacetate (1.23 g, 12 mmol) and sodium methoxide (5 drops of 10% methanolic solution) were added under stirring. The solid thus formed was filtered off and recrystallized. Yield 2.74 g (85.3%); mp 180-182°C (methanol). UV spectrum, λ_{max}, nm: 385 (3.42). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.21 (1H, s, H-7); 8.15 (1H, d, $J_{11,10}$ = 7.6, H-11); 8.13 (1H, s, H-12); 7.74 (1H, d, $J_{9,10}$ = 7.7, H-9); 7.72 (1H, t, $J_{10,11}$ = 7.6, $J_{10,9}$ = 7.7, H-10); 7.57 (1H, d, $J_{3,4}$ = 3.7, H-3); 7.51 (1H, d, $J_{4,3}$ = 3.7, H-4); 3.84 (3H, s, CO_2CH_3). ^{13}C NMR spectrum, δ, ppm: 53.6 (C-15); 97.0 (C-13); 116.4 (C-16); 119.9 (C-3); 121.9 (C-7); 124.1 (C-17); 126.5 (C-9); 127.6 (C-4); 128.9 (C-11); 129.8 (C-6); 130.8 (C-10); 130.1 (C-8); 138.9 (C-12); 148.2 (C-2); 157.5 (C-5); 163.2 (C-14). Found, %: C 59.68; H 3.22; N 4.46. $C_{16}H_{10}F_3NO_3$. Calculated, %: C 59.82; H 3.14; N 4.36.

{5-[3-(Trifluoromethyl)phenyl]-2-furyl}methylenemalononitrile (3) was prepared according to the procedure for the synthesis of **2**. Yield 81.6%; mp 143-146°C (methanol). ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.05 (2H, m, H-12, H_{arom}); 7.67 (2H, m, H_{arom}); 7.48 (1H, s, H_{arom}); 7.34 (1H, d, $J_{3,4}$ = 3.9, H-3); 7.05 (1H, d, $J_{4,3}$ = 3.9). Found, % C 62.40; H 2.34; N 9.60. $C_{15}H_7F_3N_2O$. Calculated, %: C 62.51; H 2.45; N 9.72.

(2*E*)-2-(2-Furyl)-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}acrylonitrile (4). To a solution of **1** (1.2 g, 5 mmol) and 2-furylacetonitrile (0.5 g, 5 mmol) in methanol (30 ml), sodium methoxide (5 drops of 10% methanolic solution) was added under stirring. The reaction mixture was refluxed for 1 h. After cooling the crystals formed were filtered off and recrystallized. Yield 0.88 g (53.7%); mp 97-100°C (methanol). UV spectrum, λ_{max}, nm: 398 (3.50); 288 (2.79). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.96 (1H, s, H_{arom}); 7.52 (3H, m, H_{arom}); 7.25 (1H, s, H-12); 6.84 (1H, d, H-3); 6.95 (1H, d, $J_{3,4}$ = 3.7, H-4); 6.63 (1H, d, $J_{3',4'}$ = 3.4, H-3'); 6.47 (1H, d, $J_{4',3'}$ = 3.4, H-4'); 7.41 (1H, d, $J_{4',5'}$ = 1.8, H-5'). Found, %: C 65.74; H 3.21; N 4.32. $C_{18}H_{10}F_3NO_2$. Calculated, %: C 65.66; H 3.06; N 4.25.

(2*E*)-1-Phenyl-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}prop-2-en-1-one (5). Aldehyde **1** (1.2 g, 5 mmol) was suspended in hot methanol (30 ml), acetophenone (0.52 g, 5 mmol) and NaOH (5 drops of 10% water solution) were added under stirring for 30 min. The crystals formed were filtered off and recrystallized. Yield 0.7 g (48.3%); mp 122-124°C (ethanol). UV spectrum, λ_{max}, nm: 380 (3.84); 264 (3.21). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.06-7.92 (4H, m, H_{arom}); 7.64-7.46 (4H, m, H_{arom}); 7.25 (1H, s, H_{arom}); 7.61 (1H, d, $J_{12,13}$ = 15.4, H-12); 7.52 (1H, d, $J_{13,12}$ = 15.3, H-13); 6.85 (1H, d, $J_{3,4}$ = 3.6, H-3); 6.82 (1H, d, $J_{4,3}$ = 3.6, H-4). Found, %: C 70.06; H 3.91. $C_{20}H_{13}F_3O_2$. Calculated, %: C 70.17; H 3.83.

2-Thioxo-5-{5-[3-(trifluoromethyl)phenyl]-2-furyl}methylene-1,3-thiazolidin-4-one (6). Compound **1** (2.4 g, 10 mmol) and 2-thioxo-1,3-thiazolidin-4-one (1.33 g, 15 mmol) were dissolved in glacial acetic acid (25 ml), and potassium acetate (3.5 g, 30 mmol) was added into the refluxing mixture. After 30 min the fine crystals were filtered off after cooling and washed with water, ethanol, and ether. Yield 1.53 g (43.1%); mp 239-242°C. UV spectrum, λ_{max}, nm: 430 (3.53); 304 (3.39). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 13.36 (1H, br. s, NH); 8.16 (1H, s, H-12); 8,12 (1H, s, H-7); 7.93-7.81 (3H, m, H_{arom}); 7.55 (1H, d, $J_{4,3}$ = 3.75, H-4); 7.35 (1H, d, $J_{3,4}$ = 3.75, H-3). Found, %: C 50.81; H 2.17; N 3.81. $C_{15}H_8F_3NO_2S_2$. Calculated, %: C 50.70; H 2.27; N 3.94.

2-{5-[3-(Trifluoromethyl)phenyl]-2-furyl}methylene-5,5-dimethylcyclohexane-1,3-dione (7). Aldehyde **1** (2.4 g, 10 mmol), 5,5-dimethylcyclohexane-1,3-dione (1.4 g, 10 mmol), and piperidine (5 drops) in methanol (50 ml) were refluxed for 40 min; after cooling, water was added. The crystals formed were filtered off and recrystallized; yield 1.86 g (51.05%); mp 129-131°C (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.43 (1H, d, $J_{4,3}$ = 3.9, H-4); 8.22 (2H, s, H-7, H_{arom}); 7.81 (3H, m, H_{arom}); 7.58 (1H, d, $J_{3,4}$ = 3.9); 2.63 (4H, s, CH_2); 1.03 (6H, s, $2CH_3$). Found, %: C 66.38; H 4.60. $C_{20}H_{17}F_3O_3$. Calculated, %: C 66.29; H 4.73.

Methyl 2-Azido-3-{5-[3-(trifluoromethyl)phenyl]-2-furyl}propenoate (8). A solution of compound **1** (10 g, 42 mmol) and methyl azidoacetate (19.3 g, 160 mmol) in methanol (100 ml) was added at 0°C during 30 min to a methanolic solution of sodium methoxide (7.72 g, 340 mmol of Na metal in 250 ml). Stirring was continued for an additional 60 min at a temperature not exceeding 15°C; the reaction mixture was cooled to -5°C to -10°C, a solution of ammonium chloride (8.82 g, 170 mmol) in water (42 ml) was added, and the mixture was poured in ice-cold water (250 ml). The separated precipitate was filtered off and recrystallized. Yield 6.19 g (44.1%); mp 100-104°C (methanol). UV spectrum, λ_{max}, nm: 361 (3.49). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.06 (1H, s, H-7); 8.00 (1H, d, $J_{11,10}$ = 7.6, H-11); 7.71 (1H, d, $J_{9,10}$ = 7.7, H-9); 7.67 (1H, t, $J_{10,11}$ = 7.6, $J_{10,9}$ = 7.7, H-10); 7.38 (1H, d, $J_{3,4}$ = 3.5, H-4); 7.26 (1H, d, $J_{4,3}$ = 3.5, H-3); 6.86 (1H, s, H-12); 3.84 (3H, s, CO_2CH_3). Found, %: C 53.52; H 3.11; N 12.35. $C_{15}H_{10}F_3N_3O_3$. Calculated, %: C 53.42; H 2.99; N 12.46.

Methyl 2-[3-(Trifluoromethyl)phenyl]-4H-furo[3,2-*b*]pyrrole-5-carboxylate (9). Compound **8** (6.19 g, 20 mmol) was dissolved in toluene (1 g in 100 ml). The reaction mixture was refluxed for 30 min. The crystals was separated and recrystallized. Yield 3.14 g (55.4%); mp 198-202°C (methanol). UV spectrum, λ_{max}, nm: 336 (3.57). ^{1}H NMR spectrum, δ, ppm : 11.89 (1H, s, NH); 8.01 (2H, s, H_{arom}); 7.65 (2H, d, H_{arom}); 7.42 (1H, s, H-3); 6.81 (1H, s, H-6); 3.81 (3H, s, CO_2CH_3). Found, %: C 58.28; H 3.11; N 4.48. $C_{15}H_{10}F_3NO_3$. Calculated, %: C 58.26; H 3.26; N 4.53.

5-[3-(Trifluoromethyl)phenyl]furan-2-carbaldehyde (2,6-Dimethylphenyl)hydrazone (10). To aldehyde **1** (2.4 g, 10 mmol) in toluene (25 ml) 2,6-dimethylphenylhydrazine (1.4 g, 10.2 mmol) in toluene (15 ml) and AcOH (1 ml) were added. The reaction mixture was refluxed for 3 h, the solvent was evaporated in

vacuum, and the product was recrystallized; yield 2.3 g (64.8%); mp 122-125°C (ethanol). UV spectrum, λ_{max}, nm: 350 (3.49); 208 (3.51). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.80 (1H, s, H-12); 7.88 (1H, br. s, NH); 7.43 (2H, s, H_{arom}); 7.06-7.10 (5H, br. s, H_{arom}); 6.71 (1H, d, $J_{4,3}$ = 3.5, H-4); 6.46 (1H, d, $J_{3,4}$ = 3.5, H-3); 2.33 (6H, s, $2CH_3$). Found, %: C 66.92; H 4.80; N 7.63. $C_{20}H_{17}F_3N_2O$. Calculated, %: C 67.03; H 4.78; N 7.82.

(2*E*)-3-{5-[3-(Trifluoromethyl)phenyl]-2-furyl}propenoic Acid (11). A mixture of aldehyde **1** (2.4 g, 10 mmol), malonic acid (1.04 g, 10 mmol), and pyridine was heated on a steam bath for 8 h. The reaction mixture was poured on crushed ice acidified with hydrochloric acid. The separated precipitate was filtered off, washed with water, dried, and recrystallized. Yield 2.0 g (71%); mp 210-213°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.12-7.64 (4H, m, H_{arom}); 7.42 (1H, d, $J_{3,2}$ = 15.7, H-3); 7.33 (1H, d, $J_{3',4'}$ = 3.5, H-3'); 7.05 (1H, d, $J_{4',3'}$ = 3.5, H-4'); 6.41 (1H, d, $J_{2,3}$ = 15.7, H-2). Found, %: C 59.48; H 3.36. $C_{14}H_9F_3O_3$. Calculated, %: C 59.58; H 3.21.

(2*E*)-3-{5-[3-(Trifluoromethyl)phenyl]-2-furyl}propenoic Azide (12). Acid **11** (2.82 g, 1.0 mmol) was suspended in absolute acetone (20 ml) and cooled to 0°C, and triethylamine (1.17 g, 12 mmol) was added at 0°C under stirring. Then the solution of ethyl chloroformate (1.37 g, 13 mmol) in 2 ml acetone was added dropwise, keeping the temperature below 0°C. The mixture was stirred for 30 min at 0°C; then sodium azide (1.0 g, 15 mmol) in 5 ml of water was added. The mixture was stirred for an additional hour and then poured into ice water (50 ml). The yellow precipitate was filtered off, washed with water, and dried in air. Yield 2.91 g (95%); mp 96-97°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.17 (1H, s, H_{arom}); 8.13-7.67 (3H, m, H_{arom}); 7.59 (1H, d, $J_{3,2}$ = 15.55, H-3); 7.40 (1H, d, $J_{3',4'}$ = 3.6, H-3'); 7.23 (1H, d, $J_{4',3'}$ = 3.6, H-4'); 6.52 (1H, d, $J_{2,3}$ = 15.55, H-2). Found, %: C 54.82; H 2.52; N 13.89. $C_{14}H_8F_3N_3O_2$. Calculated, %: C 54.73; H 2.62; N 13.68.

2-[3-(Trifluoromethyl)phenyl]-4,5-dihydrofuro[3,2-*c*]pyridin-4-one (13). Azide **12** (9.3 g; 33 mmol) was dissolved in dry toluene (70 ml) and added dropwise to a mixture of tributylamine (5.15 g, 28 mmol) and Dowtherm (22 ml) preliminarily heated to 180-200°C. The addition was effected at 180°C in such a way that toluene distilled off continuously. After cooling, diethyl ether was added to the mixture, and the precipitate was filtered off, washed with diethyl ether, dried, and recrystallized. Yield 4.8 g (56.8%); mp 253-254°C (ethanol). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.59 (1H, s, NH); 8.15-7.70 (5H, m, H-3, H_{arom}); 7.38 (1H, d, $J_{6,7}$ = 6.9, H-6); 6.74 (1H, d, $J_{7,6}$ = 6.9, H-7). Found, %: C 60.10; H 2.77; N 5.13. $C_{14}H_8F_3NO_2$. Calculated, %: C 60.22; H 2.89; N 5.02.

4-Chloro-2-[3-(trifluoromethyl)phenyl]furo[3,2-*c*]pyridine (14). Pyridone **13** (6.2 g, 22 mmol) was refluxed in phosphorus oxychloride (25 ml) for 4 h. $POCl_3$ was distilled off at reduced pressure, and ice was added to the residue. The mixture was then made basic with dilute aqueous ammonia. The precipitate obtained was filtered off, washed with water, and dried. The crude product was recrystallized. Yield 6 g (93.8%); mp 115-116°C (hexane). ^{1}H NMR spectrum, δ, ppm: 8.37-8.29 (4H, m, H_{arom}); 7.87-7.75 (3H, m, H-3, H_{arom}). Found, %: C 56.58; H 2.48; N 4.60. $C_{14}H_7ClF_3NO$. Calculated, %: C 56.49; H 2.37; N 4.71.

2-[3-(Trifluoromethyl)phenyl]furo[3,2-*c*]pyridine (15). Compound **14** (2.97 g, 10 mmol) was dissolved in dry ethanol (150 ml), and added by Pd/C (10%, 0.7 g) and hydrazine hydrate (7.7 ml). The mixture was refluxed for 0.5 h. The catalyst was filtered off, and ethanol was removed by reduced pressure. The crude product was recrystallized; yield 2.32 g (88.5%); mp 110-112°C (hexane). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.01 (1H, s, H-4); 8.52 (1H, d, $J_{6,7}$ = 5.8, H-6); 8.26 (1H, s, H_{arom}); 7.81-7.74 (3H, m, H_{arom}); 7.75 (1H, d, $J_{7,6}$ = 5.8, H-7); 7.05 (1H, s, H-3). Found, %: C 63.77; H 2.95; N 5.43. $C_{14}H_8F_3NO$. Calculated, %: C 63.88; H 3.06; N 5.32.

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