ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 9, pp. 1297–1303. © Pleiades Publishing, Ltd., 2016.
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Synthesis of Formyl and Carboxy Derivatives of Heterocycles by Modification of 2-(2-Aminovinyl)-benzofuran-5,6-dicarbonitriles

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Received April 15, 2016

Abstract—Procedures have been developed for the synthesis of 2-formylbenzofuran-5,6-dicarbonitriles, 5,6-dicyanobenzofuran-2-carboxylic acids, and formyldibenzo[*b*,*d*]furan-2,3-dicarbonitriles by modification of 2-(2-aminovinyl)benzofuran-5,6-dicarbonitriles with sodium periodate or Vilsmeier reagent.

DOI: 10.1134/S1070428016090074

Synthesis of various substituted 2-formylbenzofurans and benzofuran-2-carboxylic acids is a promising line of development of heterocyclic chemistry. Interest in compounds of these series is determined by their diverse pharmacological activity, in particular antitumor [1, 2] and anti-inflammatory activity [3], as well as selective cytotoxicity against cancer cells [4].

A general procedure for the synthesis of 2-formylbenzofurans is based on the oxidation of methyl group in the 2-position with SeO_2 [5–7]; another procedure involves radical oxidation of substituted vinyloxybenzenes with atmospheric oxygen in the presence of metal-free catalysts [8]. Various substituted benzofuran-2-carboxylic acids were synthesized by condensation of salicylaldehyde or its derivatives with chloroacetic acid [9, 10] or 1,1-dichloroethene [11] and by base-catalyzed ring contraction of substituted 3-bromocoumarins [12]. For preparative purposes, substituted benzofuran-2-carboxylic acids are obtained in two steps: in the first step, substituted 2-methylbenzofuran is oxidized with SeO_2 to benzofuran-2-carbaldehyde, and the aldehyde group in the latter is then converted into carboxy by the action of various oxidants [7, 13, 14].

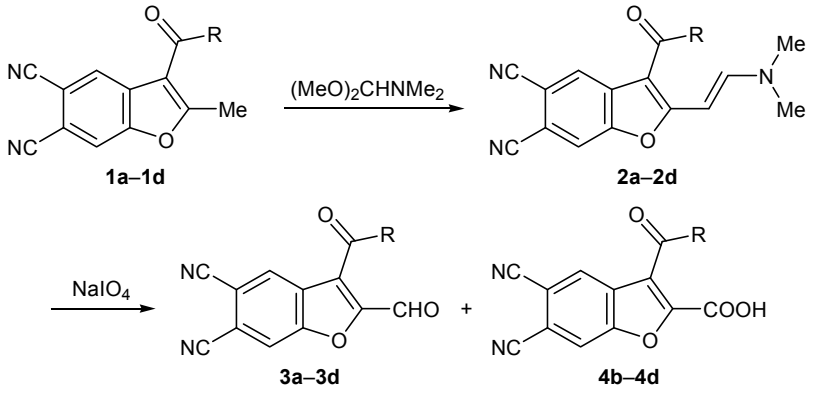
We have developed methods for the synthesis of new substituted formylbenzofuran-5,6-dicarbonitriles and 5,6-dicyanobenzofuran-2-carboxylic acids. The oxidation of 2-methylbenzofuran-5,6-dicarbonitriles [15] with SeO_2 was too slow. According to the ^{1}H NMR data, the substrate conversion in 100 h after the reaction started (in dioxane under reflux) was as low as ~2%. Therefore, it was proposed to oxidize preliminarily prepared 2-(2-aminovinyl)benzofuran-5,6-dicarbonitriles [16] with sodium periodate [17, 18].

2-[2-(Dimethylamino)ethenyl]benzofuran-5,6-dicarbonitriles **2a**–**2d** were synthesized from the corresponding 2-methylbenzofurans **1a**–**1d** [15] according to the procedure described in [16]. The reaction of 3-acetyl-2-methylbenzofuran-5,6-dicarbonitrile (**1a**) with dimethylformamide dimethyl acetal (DMF-DMA) at ~80°C involved only the 2-methyl group which is a stronger CH acid than the 3-acetyl methyl group; as a result, compound **2a** was selectively formed. Its structure was confirmed by NMR (including NOESY data) and mass spectra.

Dimethylaminovinyl derivatives **2a**–**2d** [17] were oxidized with $NaIO_4$ in 50% aqueous THF at 50–60°C (5–6 h). The products were mixtures of 2-formylbenzofuran-5,6-dicarbonitriles **3a**–**3d** and 5,6-dicyanobenzofuran-2-carboxylic acids **4b**–**4d**. Formyl derivatives **3a**–**3d** were extracted into methylene chloride, and the extract was washed with aqueous sodium hydrogen carbonate. Carboxylic acids **4b**–**4d** were isolated by acidification of the aqueous solution with HCl. The overall yield was 55–70%. Acid **4a** was not isolated, presumably due to stability of aldehyde **3a** to further oxidation (Scheme 1).

The yields of **3a**–**3d** and **4b**–**4d** and their ratio depended primarily on the reaction temperature and, to a lesser extent, on the R substituent. No oxidation was observed below 40°C, whereas raising the temperature above 60°C resulted in considerable tarring and forma-

Scheme 1.



1a–1d **2a–2d** **3a–3d** **4b–4d**

R = Me (**a**), EtO (**b**), Ph (**c**), 4-MeC_6H_4 (**d**).

tion of products which were difficult to identify. The yield of acids **4** increased as the amount of the oxidant increased; however, we failed to find conditions for the selective formation of either aldehyde **3b**–**3d** or carboxylic acid **4b**–**4d**. Presumably, the oxidation to aldehyde **3** is the rate-determining step; since aldehydes readily undergo further oxidation, the yield of **3** considerably decreases, while the corresponding acid accumulates in the reaction mixture.

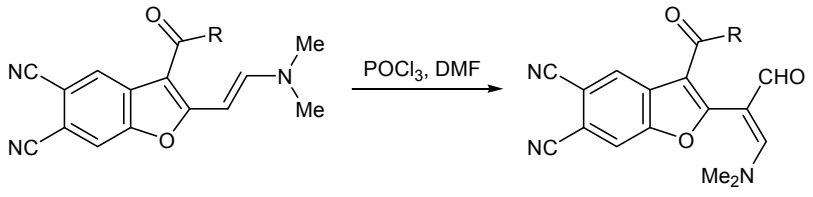
The structure of **3a**–**3d** and **4b**–**4d** was confirmed by IR, NMR, and mass spectra. The IR spectra of **3a**–**3d** characteristically contained an absorption band at 1670–1680 cm^{-1}, which is typical of aldehyde carbonyl. The aldehyde proton resonated in the ^1H NMR spectra of **3a**–**3d** at δ 9.74–10.35 ppm. No COOH proton signal was generally observed in the ^1H NMR spectra of acids **4b**–**4d** because of exchange with the solvent. The presence of a carboxy group in **4c** was confirmed by the ^{13}C NMR spectrum which displayed downfield signals of the acid carbonyl carbon atom at δ_C 158.5 ppm and ketone carbonyl at δ_C 188.6 ppm.

Alternatively, an aldehyde group can be introduced into molecules of aromatic and heterocyclic compounds by the Vilsmeier–Haack reaction. Treatment of compounds containing a methyl group with a mixture of DMF and phosphoryl chloride ($POCl_3$) leads to the formation of the corresponding formyl derivatives [19, 20]. In addition, aldehydes can be obtained by acid hydrolysis of the dimethylaminovinyl fragment of **2** [21, 22].

Benzofuran-5,6-dicarbonitriles **2c**–**2f** with an aromatic or heterocyclic R substituent reacted with $POCl_3$/DMF at 80–90°C to give previously unknown formylvinyl derivatives **5c**–**5f** (Scheme 2). A probable mechanism for the formation of structurally related compounds was described in [23, 24].

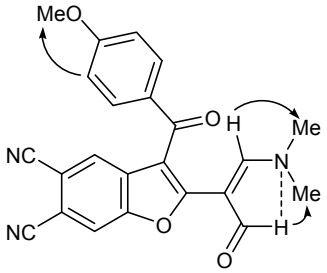
The structure of **5c**–**5f** was determined using different two-dimensional (^1H–^{13}C) NMR techniques and high resolution mass spectrometry. The ^{13}C NMR spectrum of **5e** contained two carbonyl carbon signals. Analysis of the NOESY, HMBC, and HSQC spectra of **5e** showed that the formyl group is attached to the α-carbon atom with respect to the furan ring and that the exocyclic double bond in molecule **5e** has exclusively *E* configuration. This follows from the NOESY cross peaks between the *N*-methyl protons, on the one hand, and aldehyde proton and proton at the double bond, on the other (see below). Such configuration of molecule **5e** favors intramolecular hydrogen bonding between the aldehyde proton and nitrogen atom of the aminovinyl fragment; as a result, the aldehyde proton signal is broadened.

Scheme 2.



2c–2f **5c–5f**

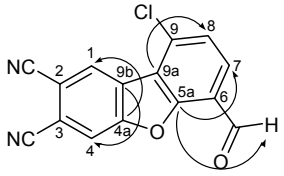
R = Ph (**c**), 4-MeC_6H_4 (**d**), 4-$MeOC_6H_4$ (**e**), thiophen-2-yl (**f**).



5e

Compound **2a** reacted with 3 equiv of Vilsmeier reagent in a different way (Scheme 3). Apart from the 2-methyl group, the reaction at 40–90°C involved the 3-acetyl group of **2a** and afforded a mixture of mono- and diformyldibenzo[*b*,*d*]furan-2,3-dicarbonitriles **6** and **7**, the former prevailing. When the reaction was carried out at room temperature, compound **6** was isolated as the major product. Likewise, the reaction of **1a** with Vilsmeier reagent gave a mixture of **6** and **7**. The product ratio depended on the amount of Vilsmeier reagent, temperature, and reaction time. Increase of the amount of $POCl_3$ to 10 equiv, temperature to 90°C, and reaction time to 6 h favored formation of dialdehyde **7** whose yield attained 50%. However, we failed to find conditions for the selective formation of **7**. Aldehyde **6** was converted into hydrazone **8** by treatment with hydrazine hydrate and reduced to alcohol **9** with $NaBH_4$ (Scheme 4).

The structure of **6** and **7** was confirmed by IR, NMR, and mass spectra. The structure of **6** was unambiguously determined by analysis of two-dimensional $^{1}H–^{13}C$ correlation spectra (HSQC, HMBC). Other possible structures were ruled out by the presence of strong C^{4a}/1-H and C^{5a}/7-H strong peaks, as well as of weak C^{5a}/C**H**O correlation.

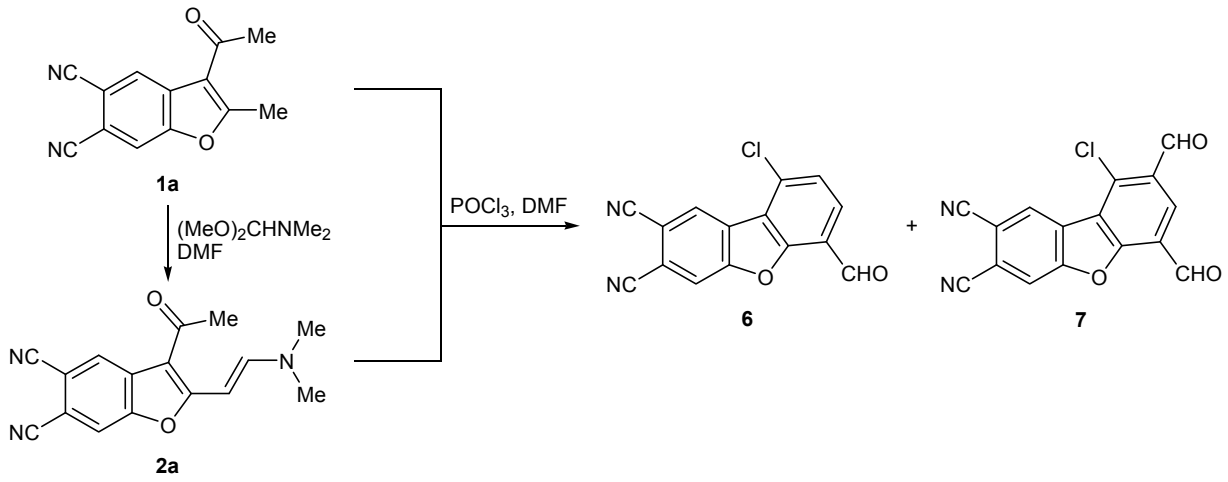


6

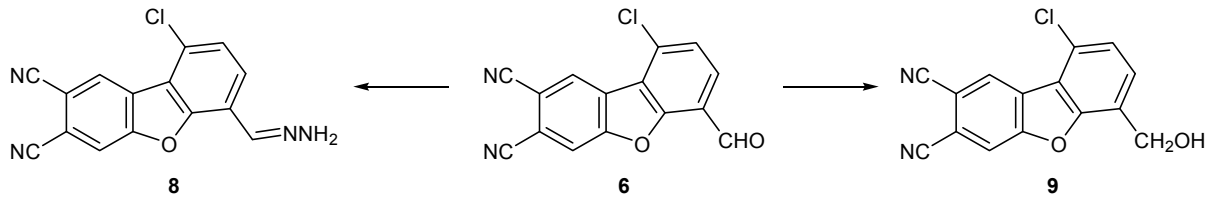
The formation of dibenzofurancarbaldehydes **6** and **7** from substituted benzofurans is the most remarkable result of our experiments since compounds of this sort are commonly synthesized by formylation of preliminarily prepared dibenzofurans [25], oxidation of hydroxymethyl-substituted dibenzofurans [26], or intramolecular cyclization of phenols containing a formyl group [27, 28].

Scheme 5 shows a probable mechanism of formation of compounds **6** and **7**. 3-Acetyl-2-methylbenzofuran-5,6-dicarbonitrile (**1a**) reacts with $POCl_3$/DMF to give dimethylaminovinyl derivative **2a**. Further reaction of **2a** with Vilsmeier reagent leads to diaminovinyl intermediate **A**. Analogous intermediate derived

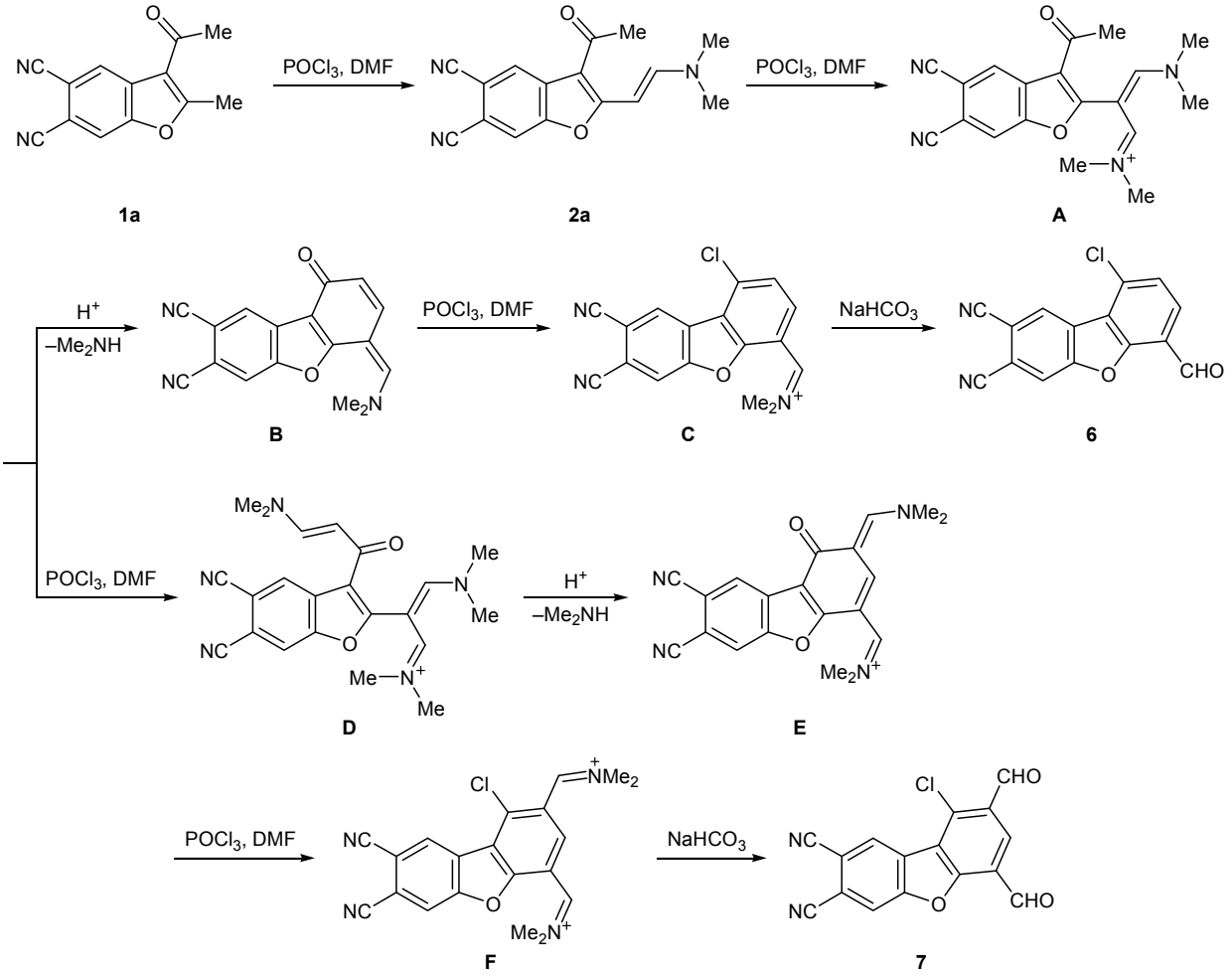
Scheme 3.



Scheme 4.



Scheme 5.



from **2c**–**2f** is then converted into aldehydes **5c**–**5f**. In the reactions with **1a** (**2a**), the subsequent transformations of intermediate **A** follow two pathways. The first pathway involves intramolecular cyclization to dihydrodibenzofuran structure **B** with elimination of dimethylamine, replacement of the carbonyl oxygen atom by chlorine, and hydrolysis of intermediate **C** to aldehyde **6** with aqueous sodium hydrogen carbonate. Alternatively, further reaction of **A** with Vilsmeier reagent at the acetyl group leads to intermediate **D** whose cyclization to dihydrodibenzofuran **E** is followed (as in the first pathway) by aromatization and chlorination with formation of intermediate **F** as precursor to dicarbaldehyde **7**.

EXPERIMENTAL

The IR spectra (700–4000 cm^{-1}) were recorded in mineral oil on a Perkin Elmer RX-1 spectrometer with Fourier transform. The NMR spectra were measured on a Bruker DRX-400 or Bruker DRX-500 instrument at 30°C using DMSO-d_6 as solvent and reference (DMSO-d_5, δ 2.50 ppm; DMSO-d_6, δ_C 39.5 ppm). The two-dimensional NMR spectra were recorded using Bruker standard pulse sequences; NOESY mixing time 0.3 s.

The mass spectra were taken on a Finnigan MAT INCOS 50 mass spectrometer coupled with a gas chromatograph and on a Kratos MS-30 high-resolution mass spectrometer (UK); electron impact, 70 eV; ion source temperature 100–220°C. The NMR and mass spectral studies were performed at the Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences (Moscow, Russia).

The elemental analyses were obtained on a Perkin Elmer 2400 analyzer at the Analytical Laboratory (Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia). The melting points were determined using a DSK-5500 differential scanning calorimeter or a Büchi M-560 melting (boiling) point apparatus.

Compounds 3a–3d and 4b–4d (*general procedure*). Compound **2a**–**2d**, 2 mmol, was dissolved in 5 mL of 50% aqueous THF, 1.5 g (7 mmol) of $NaIO_4$ was added, and the mixture was stirred for 5–6 h at 50–60°C (TLC). The mixture was cooled, 20 mL of 10% aqueous sodium hydrogen carbonate was added, the mixture was extracted with methylene chloride, the extract was subjected to silica gel chromatography, the eluate was evaporated, and the precipitate was filtered off and dried. We thus isolated compounds **3a**–**3d**. The aqueous phase obtained after extraction was acidified to pH 2–3 with aqueous HCl, and the precipitate of **4b**–**4d** was filtered off, washed with water, and dried.

3-Acetyl-2-formyl-1-benzofuran-5,6-dicarbonitrile (3a). Yield 0.081 g (17%), mp 170–171°C. IR spectrum, ν, cm^{-1}: 2231 (CN), 1680 (C=O), 1604 (C=C), 1280 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.87 s (3H, CH_3), 8.87 s (1H, 7-H), 8.93 s (1H, 4-H), 10.25 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 31.60 (Me), 110.89, 113.36, 115.66 (CN), 115.79 (CN), 119.93, 125.20, 128.89, 153.71, 154.70, 167.07, 181.04 (CHO), 193.22 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 238 (37) $[M]^+$, 195 (100), 43 (35). Found, %: C 65.39; H 2.43; N 11.74. $C_{13}H_6N_2O_3$. Calculated, %: C 65.55; H 2.54; N 11.76. *M* 238.20.

Ethyl 5,6-dicyano-2-formyl-1-benzofuran-3-carboxylate (3b). Yield 0.11 g (20%), mp 234–236°C. IR spectrum, ν, cm^{-1}: 2235 (CN), 1712 (C=O), 1681 (C=O), 1600 (C=C), 1287 (C–O–C). ^1H NMR spectrum, δ, ppm: 1.43 t (3H, CH_3, J = 7.1 Hz), 4.50 q (2H, CH_2, J = 7.1 Hz), 8.80 s (1H, 7-H), 8.90 s (1H, 4-H), 10.37 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 268 (20) $[M]^+$, 254 (14), 239 (33) $[M - COH]^+$, 226 (25), 223 (21), 212 (64), 195 (98) $[M - COOEt]^+$, 168 (44), 139 (100), 88 (26), 87 (30). Found, %: C 62.42; H 2.96; N 10.41. $C_{14}H_8N_2O_4$. Calculated, %: C 62.69; H 3.01; N 10.44. *M* 268.23.

3-Benzoyl-2-formyl-1-bezofuran-5,6-dicarbonitrile (3c). Yield 0.22 g (36%), mp 216–218°C. IR spectrum, ν, cm^{-1}: 2238 (CN), 1677 (C=O), 1655 (C=O), 1596 (C=C), 1296 (C–O–C). ^1H NMR spectrum, δ, ppm: 7.61 t (2H, *o*-H, J = 7.8 Hz), 7.79 t (1H, *p*-H, J = 7.5 Hz), 7.61 d (2H, *m*-H, J = 7.8 Hz), 8.48 s (1H, 7-H), 8.94 s (1H, 4-H), 9.74 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 300 (100) $[M]^+$, 271 (22) $[M - COH]^+$, 244 (51), 215 (27), 195 (21), 139 (24), 105 (30), 77 (85). Found, %: C 71.73; H 2.65; N 9.29. $C_{18}N_8N_2O_3$. Calculated, %: C 72.00; H 2.69; N 9.33. *M* 300.28.

2-Formyl-3-(4-methylbenzoyl)-1-benzofuran-5,6-dicarbonitrile (3d). Yield 0.21 g (34%), mp 215–217°C. IR spectrum, ν, cm^{-1}: 2237 (CN), 1679 (C=O), 1650 (C=O), 1598 (C=C), 1290 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.44 s (3H, CH_3), 7.41 d (2H, *o*-H, J = 8.1 Hz), 7.87 d (2H, *m*-H, J = 8.1 Hz), 8.49 s (1H, 7-H), 8.93 s (1H, 4-H), 9.76 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 314 (43) $[M]^+$, 271 (13), 195 (9), 139 (34), 119 (14), 91 (100), 65 (70). Found, %: C 72.43; H 3.19; N 8.89. $C_{19}H_{10}N_2O_3$. Calculated, %: C 72.61; H 3.21; N 8.91. *M* 314.30.

5,6-Dicyano-3-(ethoxycarbonyl)-1-benzofuran-2-carboxylic acid (4b). Yield 0.20 g (35%), mp 244–246°C. ^1H NMR spectrum, δ, ppm: 1.12 t (3H, CH_3, J = 7.0 Hz), 4.17 q (2H, CH_2, J = 7.0 Hz), 8.69 s (1H, 7-H), 8.79 s (1H, 4-H); no OH proton signal was observed because of exchange. Found, %: C 59.03; H 2.81; N 9.84. $C_{14}H_8N_2O_5$. Calculated, %: C 59.16; H 2.84; N 9.86.

3-Benzoyl-5,6-dicyano-1-benzofuran-2-carboxylic acid (4c). Yield 0.19 g (30%), mp 210–212°C. IR spectrum, ν, cm^{-1}: 3505 (OH), 2237 (CN), 1724 (C=O), 1641 (C=O), 1597 (C=C), 1278 (C–O–C). ^1H NMR spectrum, δ, ppm: 7.55 t (2H, *o*-H, J = 7.5 Hz), 7.72 t (1H, *p*-H, J = 7.5 Hz), 7.91 d (2H, *m*-H, J = 7.5 Hz), 8.56 s (1H, 7-H), 8.88 s (1H, 4-H); no OH proton signal was observed because of exchange. ^{13}C NMR spectrum, δ_C, ppm: 110.4, 112.8, 115.8, 116.0, 119.9, 124.3, 129.0, 129.3, 129.6, 130.3, 134.5, 136.3, 147.9, 154.1, 158.5, 188.6. Mass spectrum, *m*/*z* (I_{rel}, %): 316 (100) $[M]^+$, 272 (30), 271 (34), 244 (60), 239 (49), 105 (38), 77 (35). Found, %: C 68.18; H 2.50; N 8.81. $C_{18}H_8N_2O_4$. Calculated, %: C 68.36; H 2.55; N 8.86. *M* 316.28.

5,6-Dicyano-3-(4-methylbenzoyl)-1-benzofuran-2-carboxylic acid (4d). Yield 0.22 g (34%), mp 219–221°C. IR spectrum, ν, cm^{-1}: 3513 (OH), 2223 (CN), 1728 (C=O), 1638 (C=O), 1603 (C=C), 1286 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.40 s (3H, CH_3), 7.35 d (2H, *o*-H, J = 8.1 Hz), 7.81 d (2H, *m*-H, J = 8.1 Hz), 8.51 s (1H, 7-H), 8.87 s (1H, 4-H); no OH proton signal was observed because of exchange. Mass spectrum, *m*/*z* (I_{rel}, %): 330 (6) $[M]^+$, 139 (17), 119 (31), 91 (100), 65 (63). Found, %: C 68.84; H 3.00; N 8.43. $C_{19}H_{10}N_2O_4$. Calculated, %: C 69.09; H 3.05; N 8.48. *M* 330.30.

Compounds 5c–5f (*general procedure*). Compound **2c**–**2f**, 1 mmol, was added to a solution of 0.46 g (3 mmol) of $POCl_3$ in 3 mL of DMF, and the mixture was stirred for 3 h at 80–90°C, cooled, and

poured into a cold 5% solution of $NaHCO_3$. The precipitate was filtered off, thoroughly washed with water, and dried in air.

3-Benzoyl-2-[(1*E*)-1-(dimethylamino)-3-oxoprop-1-en-2-yl]-1-benzofuran-5,6-dicarbonitrile (5c). Yield 0.31 g (84%), mp 238–240°C (decomp.). IR spectrum, ν, cm^{-1}: 2224 (CN), 1646 (C=O), 1621 (C=C), 1269 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.79 br.s [6H, $N(CH_3)_2$], 7.57 d (2H, *o*-H, *J* = 7.6 Hz), 7.70 t (1H, *p*-H, *J* = 7.6 Hz), 7.73 d (2H, *m*-H, *J* = 7.6 Hz), 8.00 s (2H, 7-H, NCH=), 8.33 s (1H, 4-H), 8.75 s (1H, CHO). Found, %: C 71.36; H 4.07; N 11.31. $C_{22}H_{15}N_3O_3$. Calculated, %: C 71.54; H 4.09; N 11.38.

2-[(*E*)-1-(Dimethylamino)-3-oxoprop-1-en-2-yl]-3-(4-methylbenzoyl)benzofuran-5,6-dicarbonitrile (5d). Yield 0.35 g (90%), mp 243–245°C (decomp.). IR spectrum, ν, cm^{-1}: 2226 (CN), 1667 (C=O), 1619 (C=C), 1258 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 7.26 d (2H, *m*-H, *J* = 7.93 Hz), 7.59 s (1H, NCH=), 7.60 d (2H, *o*-H, *J* = 7.93 Hz), 8.32 s (1H, 7-H), 8.61 s (1H, 4-H), 8.63 s (1H, CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 383 (3) $[M]^+$, 355 (5) $[M - 28]^+$, 119 (80), 91 (100). Found, %: C 71.87; H 4.43; N 10.94. $C_{23}H_{17}N_3O_3$. Calculated, %: C 72.05; H 4.47; N 10.96. *M* 383.41.

2-[(*E*)-1-(Dimethylamino)-3-oxoprop-1-en-2-yl]-3-(4-methoxybenzoyl)benzofuran-5,6-dicarbonitrile (5e). Yield 0.37 g (93%), mp 254–256°C (decomp.). IR spectrum, ν, cm^{-1}: 2227 (CN), 1664 (C=O), 1618 (C=C), 1256 (C–O–C). ^1H NMR spectrum, δ, ppm: 2.94 s and 3.29 s (3H each, NCH_3), 3.82 s (3H, OCH_3), 6.96 d (2H, *m*-H, *J* = 8.80 Hz), 7.58 s (1H, NCH=), 7.66 d (2H, *o*-H, *J* = 8.80 Hz), 8.27 s (1H, 7-H), 8.58 s (1H, 4-H), 8.65 br.s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 40.12 and 46.88 (NMe), 55.49 (OMe), 100.73 (**C**CHO), 109.09 (C^5), 109.58 (C^6), 113.31 (C^m) 116.33 (CN), 116.41 (CN), 117.34 (C^3), 117.81 (C^4), 126.94 (C^7), 130.40 (C^i), 131.12 (C^o), 132.40 (C^{3a}), 153.35 (C^{7a}), 158.47 (C^2), 161.31 (NCH=), 162.86 (C^p), 184.50 (CHO), 188.01 (C=O). Mass spectrum: *m*/*z* 422.1111. Calculated: $[M + Na]^+$ 422.1117.

2-[(*E*)-1-(Dimethylamino)-3-oxoprop-1-en-2-yl]-3-(thiophen-2-ylcarbonyl)benzofuran-5,6-dicarbonitrile (5f). Yield 0.29 g (76%), mp 216–218°C (decomp.). IR spectrum, ν, cm^{-1}: 2231 (CN), 1659 (C=O), 1618 (C=C), 1265 (C–O–C). ^1H NMR spectrum, δ, ppm: 3.00 s and 3.35 s (3H each, NMe), 7.14 d.d (1H, 4′-H, *J* = 4.9, 3.9 Hz), 7.58 br.d (1H, 3′-H, *J* = 3.9 Hz), 7.72 s (1H, NCH=), 7.99 d (1H, 5′-H, *J* = 4.9 Hz), 8.31 s (1H, 7-H), 8.58 s (1H, 4-H), 8.75 br.s (1H, CHO). Found, %: C 62.75; H 3.47; N 11.15. $C_{20}H_{13}N_3O_3S$. Calculated, %: C 63.99; H 3.49; N 11.19.

9-Chloro-6-formyldibenzo[*b*,*d*]furan-2,3-dicarbonitrile (6). Compound **2a**, 0.28 g (1 mmol), was added to a solution of 0.46 g (3 mmol) of $POCl_3$ in 3 mL of DMF, and the mixture was stirred for 3 h at room temperature and poured into a cold 5% solution of $NaHCO_3$. The precipitate was filtered off, thoroughly washed with water, and dried in air. Yield 0.24 g (85%), mp 287–289°C (decomp.). IR spectrum, ν, cm^{-1}: 2232 (CN), 1702 (C=O), 1598 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 7.73 d (1H, 8-H, *J* = 7.9 Hz), 8.14 d (1H, 7-H, *J* = 7.9 Hz), 8.75 s (1H, 4-H), 8.84 s (1H, 1-H), 10.29 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 110.24 (C^2), 113.81 (C^3), 115.57 (2-CN), 115.62 (3-CN), 118.67 (C^4), 120.22 (C^6), 120.54 (C^{9a}), 125.23 (C^8) 125.53 (C^{9b}), 128.04 (C^1), 132.97 (C^7), 134.03 (C^9), 155.46 (C^{5a}), 156.10 (C^{4a}), 187.52 (CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 280 (74) $[M]^+$, 279 (100), 252 (7) $[M - 27]^+$, 225 (31), 223 (92), 189 (44), 140 (31), 111 (38), 86 (39). Found, %: C 64.01; H 1.76; N 9.97. $C_{15}H_5ClN_2O_2$. Calculated, %: C 64.19; H 1.80; N 9.98. *M* 280.67.

Compounds 6 and 7. Compound **2a**, 0.28 g (1 mmol), or **1a**, 0.22 g (1 mmol), was added to a solution of 0.46 g (3 mmol) of $POCl_3$ in 3 mL of DMF. The mixture was stirred for 3 h at 40–90°C, cooled, and poured into a cold 5% solution of $NaHCO_3$. The precipitate was filtered off and recrystallized 3–4 times from dioxane to accumulate compound **7**, and the product was dried in air.

9-Chloro-6,8-diformyldibenzo[*b*,*d*]furan-2,3-dicarbonitrile (7). Yield 0.05 g (16%), mp >300°C (decomp.). IR spectrum, ν, cm^{-1}: 2234 (CN), 1701 (C=O), 1596 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 8.68 s (1H, 7-H), 8.96 s (1H, 4-H), 9.22 s (1H, 1-H), 10.40 s (1H, 6-CHO), 10.49 s (1H, 8-CHO). Mass spectrum, *m*/*z* (I_{rel}, %): 308 (100) $[M]^+$, 281 (41), 252 (17), 223 (92), 189 (39), 140 (29). Found, %: C 61.97; H 1.59; N 9.05. $C_{16}H_5ClN_2O_3$. Calculated, %: C 62.26; H 1.63; N 9.08. *M* 307.99.

9-Chloro-6-(hydrazinylidenemethyl)dibenzo-[*b*,*d*]furan-2,3-dicarbonitrile (8). Hydrazine hydrate, 0.10 mL (2 mmol), was added to a solution of 0.28 g (1 mmol) of compound **6** in 3 mL of ethanol, and the mixture was heated for 2 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed with ethanol, and dried in air. Yield 0.24 g (70%), mp >400°C. IR spectrum, ν, cm^{-1}: 3297 (NH),

2235 (CN), 1587 (C=C_{arom}). ^{1}H NMR spectrum, δ, ppm: 7.46 s (2H, NH_2), 7.51 d (1H, 8-H, J = 8.3 Hz), 7.83 d (1H, 7-H, J = 8.3 Hz), 8.04 s (1H, 4-H), 8.71 s (1H, 1-H), 8.89 s (1H, NH). Found, %: C 60.98; H 2.35; N 18.98. $C_{15}H_7ClN_4O$. Calculated, %: C 61.14; H 2.39; N 19.01.

9-Chloro-6-(hydroxymethyl)dibenzo[*b,d*]furan-2,3-dicarbonitrile (9). Compound **6**, 0.28 g (1 mmol), was dissolved in 3 mL of ethanol, 0.11 g (3 mmol) of $NaBH_4$ was added, and the mixture was stirred for 1.5 h at 40°C. The mixture was cooled, and the precipitate was filtered off, washed with ethanol, and dried in air. Yield 0.18 g (63%), mp >400°C. ^{1}H NMR spectrum, δ, ppm: 4.89 s (2H, CH_2), 5.66 br.s (1H, OH), 7.61 d (1H, 8-H, J = 7.9 Hz), 7.77 d (1H, 7-H, J = 7.9 Hz), 8.79 s (1H, 4-H), 8.98 s (1H, 1-H). ^{13}C NMR spectrum, δ_C, ppm: 56.97, 109.60, 113.04, 115.92, 116.01, 118.41, 124.91, 126.22, 126.25, 126.59, 127.90, 129.70, 154.62, 155.77, 166.39. Mass spectrum, m/z (I_{rel}, %): 282 (21) $[M]^+$, 281 (36) $[M]^+$, 280 (74) $[M]^+$, 279 (100) $[M - H]^+$, 225 (31), 233 (93), 189 (45), 188 (39), 140 (31), 135 (24), 111 (39), 86 (38). Found, %: C 63.61; H 2.48; N 9.87. $C_{15}H_7ClN_2O_2$. Calculated, %: C 63.73; H 2.50; N 9.91. M 282.69.

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