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Reactions of naphthalen-2-ol Mannich bases with β-aminoacrylonitriles and methyl 3-morpholinoacrylate

Anton V. Lukashenko[1], Dmitry V. Osipov[1], Vitaly A. Osyanin[1]*, Yuri N. Klimochkin[1]

[1] *Samara State Technical University, 244 Molodogvardeyskaya St., Samara 443100, Russia; e-mail: VOsyanin@mail.ru*

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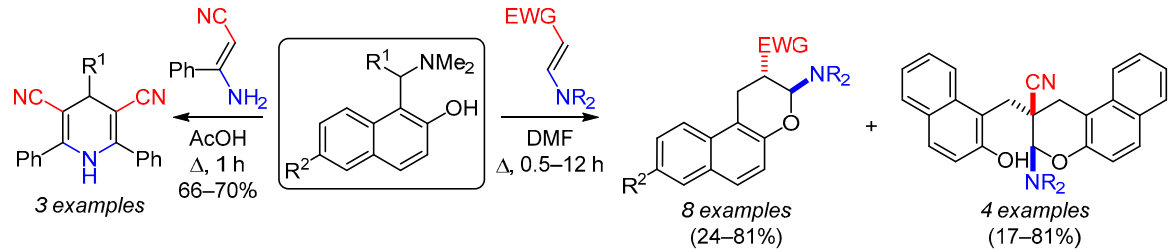


R^1 = H, Ph, 3-$O_2NC_6H_4$; R^2 = H, Br, 1-Ad; EWG = CN, CO_2Me; NR_2 = NEt_2, NPh_2, pyrrolidin-1-yl, piperidin-1-yl, morpholin-4-yl

3-Amino-2,3-dihydro-1*H*-benzo[*f*]chromenes and 2-[(2-hydroxynaphthalen-1-yl)methyl]-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles were obtained *via* the reaction of naphthalen-2-ol Mannich bases with β-aminoacrylonitriles and methyl 3-morpholinoacrylate as products of [4+2] cycloaddition of push-pull olefins to the corresponding 1,2-naphthoquinone 1-methide. The reaction of 3-amino-3-phenylacrylonitrile with Mannich bases leads to the formation of 1,4-dihydropyridine-3,5-dicarbonitriles.

Keywords: 2,3-dihydro-1*H*-benzo[*f*]chromene, 1,4-dihydropyridine, naphthalen-2-ol, 1,2-naphthoquinone 1-methide, push-pull olefin, Diels–Alder reaction.

Push-pull enamines R_2N–C=C–EWG, where EWG is an electron-withdrawing group, are widely used in the synthesis of heterocycles. This is due to the high polarization[1] of the C=C bond and the presence of several nonequivalent electrophilic and nucleophilic centers within the structure.[2] At the same time, similar enamines are rarely used as two-carbon synthons for the construction of six-membered heterocycles.[3]

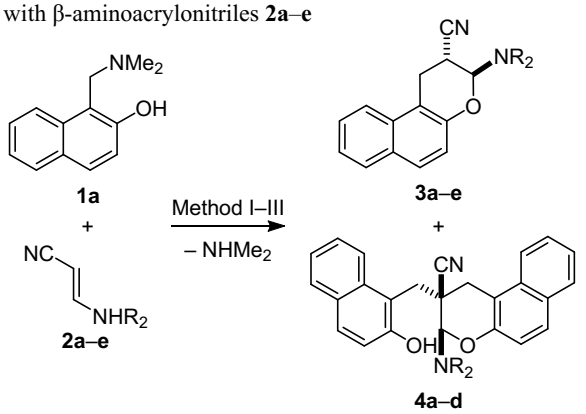
One of the main reactions that *o*-quinone methides enter into is the Diels–Alder reaction.[4] The products of this reaction, substituted chromanes and chromenes, in many cases attract much more interest than noncondensed 4*H*-pyrans.[5] To date, no method to synthesize chromane systems with a wide range of substituents has been developed, and the existing methods are often applicable only to a narrow range of substrates and require hard-to-access and expensive reagents and catalysts. At the same time, however, the presence of diverse functional groups in such systems makes them promising precursors for both further chemical transformations and research in medicinal chemistry. In addition, the relevance of developing novel methods for the synthesis of chromane and chromene derivatives is dictated by the presence of a large number of natural and biologically active compounds among them.[6]

When trying to carry out the reaction between 1-[(dimethylamino)methyl]naphthalen-2-ol (**1a**) and various β-aminoacrylonitriles **2a**–**e** in aprotic solvents (MeCN, 1,4-dioxane) or in AcOH, unsatisfactory results were obtained. In aprotic solvents, the reaction does not take place, whereas in AcOH a complex mixture of unidentified products forms. At the same time, heating equimolar amounts of β-aminoacrylonitriles **2a**–**e** and Mannich base **1a** under reflux in DMF for 1 h (method I) afforded mixtures of benzochromane-2-carbonitriles **3a**–**d** and 2-[(2-hydroxynaphthalen-1-yl)methyl]-2,3-dihydro-1*H*-benzo[*f*]-chromene-2-carbonitriles **4a**–**d**, which were preparatively separated by column chromatography (Table 1).

When 2 equiv of Mannich base **1a** was subjected to a reaction with enaminonitriles **2a**–**c** (Table 1, method II), the yields of products **3a**–**c** decrease as expected, but benzochromanes **3a**–**c** do not disappear completely, even increasing the reaction time to 12 h. At the same time, upon a slow addition of an equimolar amount of Mannich base **1a** to a DMF solution of nitrile **2a**–**d** heated to 150°C (method III), benzochromane-2-carbonitriles **3a**–**d** selectively are formed.

The reaction mechanism, apparently, involves the generation of reactive 1,2-naphthoquinone 1-methide **A** *via*

Table 1. Yields of the products of the reaction of Mannich base **1a** with β-aminoacrylonitriles **2a**–**e**



2–**4** **a** NR_2 = NEt_2, **b** NR_2 = pyrrolidin-1-yl, **c** NR_2 = piperidin-1-yl, **d** NR_2 = morpholin-4-yl, **e** NR_2 = NPh_2

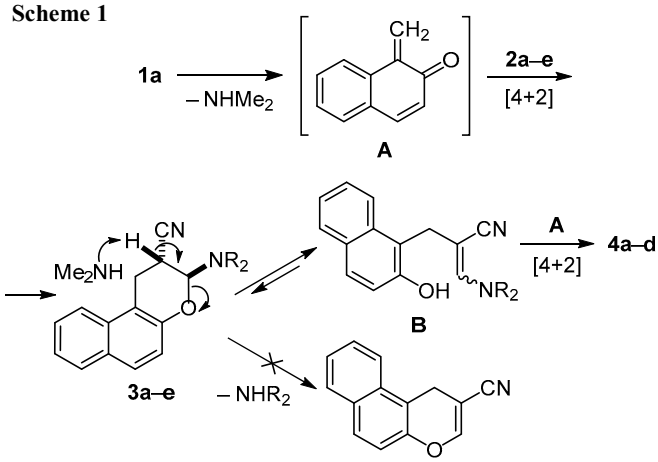
Method*	Product yields, %				
	3a / **4a**	**3b** / **4b**	**3c** / **4c**	**3d** / **4d**	**3e** / **4e**
I	41 / 18	43 / 17	46 / 15	52 / 16	78 / –
II	24 / 54	29 / 51	30 / 48	–	–
III	72 / –	80 / –	83 / –	84 / –	–
IV	–	– / 23	–	–	–
V	–	– / 81	– / 77	– / 74	–

* Method I: naphthalen-2-ol **1a** (300 mg, 1.5 mmol), nitrile **2a**–**e** (1.5 mmol), DMF, reflux, 1 h.
Method II: naphthalen-2-ol **1a** (600 mg, 3 mmol), nitrile **2a**–**c** (1.5 mmol), DMF, reflux, 1 h.
Method III: naphthalen-2-ol **1a** (300 mg, 1.5 mmol) was added to a solution of nitrile **2a**–**d** (1.5 mmol) in DMF at 150°C over 30 min.
Method IV: benzochromane **3b** (278 mg, 1.0 mmol), naphthalen-2-ol **1a** (200 mg, 1.0 mmol), DMF, reflux, 12 h.
Method V: benzochromane **3b**–**d** (1.0 mmol), naphthalen-2-ol **1a** (200 mg, 1.0 mmol), piperidine (0.1 ml, 1.0 mmol), DMF, reflux, 1 h.

thermolysis of Mannich base **1a** followed by [4+2] cycloaddition of enaminonitrile **2a**–**e** to it as the dienophile. It should be noted that push-pull enaminonitriles rarely play the role of the dienophile.[3f] Benzochromanes **4a**–**d** are probably formed as a result of the opening of the dihydropyran ring by the action of $NHMe_2$, the source of which is the starting Mannich base **1a**, and addition of another molecule of 1,2-naphthoquinone 1-methide **A** to the resulting push-pull olefin **B**. Moreover, the second equivalent of 1,2-naphthoquinone 1-methide **A**, necessary for the formation of product **4a**–**d**, is most likely formed directly from Mannich base **1a**, rather than as a result of retro-Diels–Alder reaction from cycloadduct **3a**–**d** (Scheme 1). It is interesting to note that the elimination of the secondary amine from the initial cycloadducts characteristic of derivatives containing an acyl, formyl, or nitro group in the β-position of the dihydropyran ring[3a–e] is not observed in this case. The absence of product **4e** with diphenylamino group can be explained by steric factors.

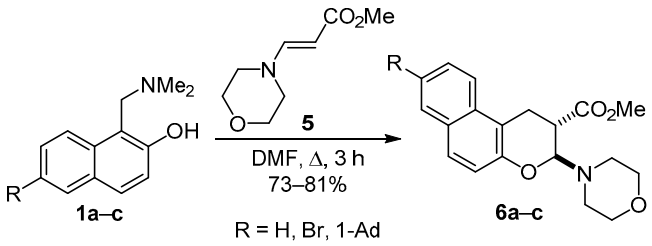
Benzochromanes **4b**–**d** were also obtained in high yields upon heating 3-amino-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles **3b**–**d** with an equimolar amount of Mannich base **1a** under reflux in DMF in the presence of 1 equiv of piperidine as the base facilitating the opening of the dihydropyran ring in compounds **3b**–**d** (Table 1, method V). The more volatile $NHMe_2$ generated from Mannich base **1a** turned out to be less effective, and as a result of prolonged heating under reflux in DMF in the absence of piperidine, product **4b** was isolated only in 23% yield (method IV).

Scheme 1



A similar reaction of methyl 3-morpholinoacrylate (**5**) with naphthalen-2-ol Mannich bases **1a**–**c** leads to the formation of cycloadducts **6a**–**c** containing no products with two naphthalene fragments as impurities even when using 2 equiv of Mannich base **1a**–**c** (Scheme 2).

Scheme 2



The IR spectra of compounds **3a**–**e** contain a low-intensity absorption band of the CN group in the region of 2241–2251 cm^{-1}, whereas the absorption band of the C=O group in the spectra of compounds **6a**–**c** appears at 1732–1734 cm^{-1}. In the ^1H NMR spectra of compounds **3a**–**d** and **6a**–**c**, the 3-CH proton signal appears at 4.86–5.01 ppm in the form of a doublet with $^3J_{H(2)–H(3)}$ = 9.2 Hz (in the case of compound **3e**, a doublet is observed at 4.74 ppm with $^3J_{H(2)–H(3)}$ = 9.8 Hz), which is typical for *trans*-2,3-disubstituted chromanes.[7] The formation of such diastereomers is most likely a consequence of the *trans* configuration of the starting olefins. The signals of the 1-CH_2 and 2-CH protons in the spectra of compounds **3a**–**d** and **6a**–**c** are observed in

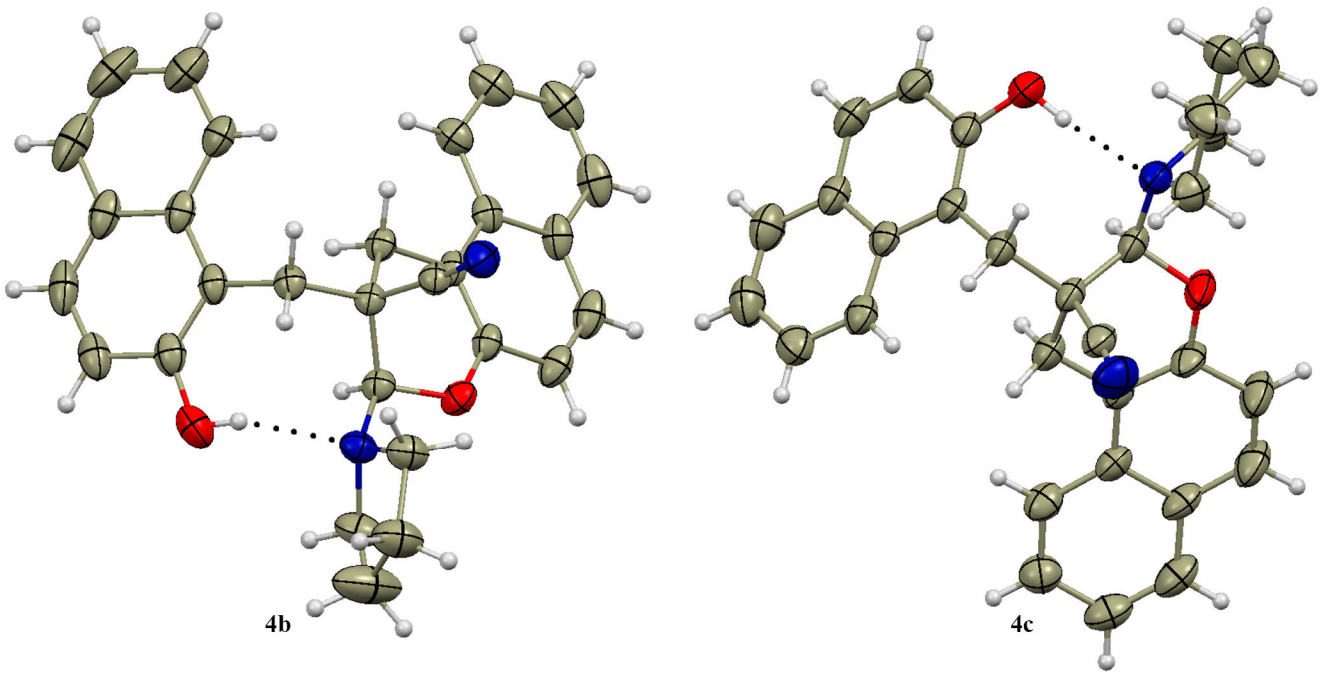


Figure 1. Molecular structures of compounds **4b**,**c** with atoms represented as thermal vibration ellipsoids of 30% probability (dotted lines indicate intramolecular hydrogen bonds).

the 3.15–3.72 ppm range in the form of complex multiplets. In the ^{13}C NMR spectra of compounds **3a**–**d** and **6a**–**c**, the C-1 atom resonates at 26.3–27.9 ppm, the C-2 atom – at 28.7–30.0 ppm (in the case of nitriles **3a**–**e**), and 40.9–42.0 ppm (in the case of esters **6a**–**c**), whereas the signal in the 85.3–93.6 ppm range can be attributed to the C-3 atom. In the ^{13}C NMR spectra of esters **6a**–**c**, the carbon atom of the C=O group appears at 172.9–175.6 ppm; in the spectra of compounds **3a**–**e**, the carbon atom of the CN group is observed in the region of 119.2–119.9 ppm.

The IR spectra of benzochromanes **4a**–**d** contain a number of absorption bands in the 3000–3400 cm^{-1} range, corresponding to vibrations of O–H bonds, and a weak-intensity absorption band in the region of 2232–2236 cm^{-1}, corresponding to the CN group. In the ^{1}H NMR spectra of compounds **4a**–**d**, OH protons and 3-CH protons resonate as singlets in the 10.15–11.22 and 4.29–5.26 ppm ranges, respectively. The ^{13}C NMR spectra of compounds **4a**–**d** are characterized by the signals of two CH_2 groups at correspondingly 28.8–30.4 and 35.5–36.8 ppm, as well as C-2 and C-3 atoms at 39.2–40.9 and 91.2–95.4 ppm, respectively.

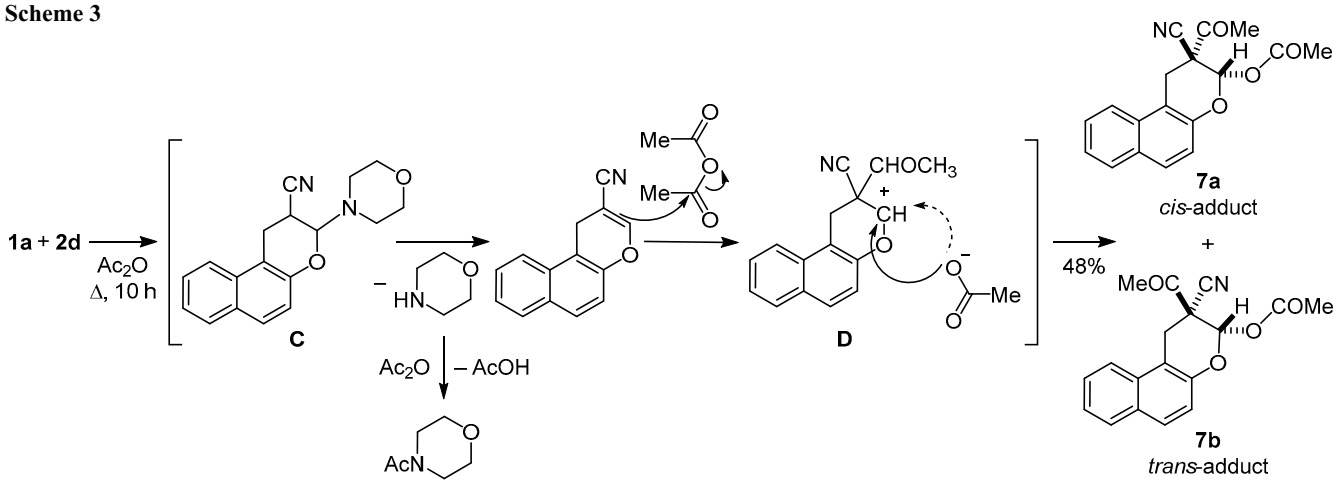
The structures of benzochromanes **4b**,**c** were confirmed by X-ray structural analysis data (Fig. 1). According to X-ray structural analysis data, an intramolecular hydrogen bond is formed between the hydrogen atom of the OH group and the nitrogen atom of the amino group, the length of which is 2.051 Å (compound **4b**) and 1.935 Å (compound **4c**).

A slightly different type of transformation is observed upon heating of 1-[(dimethylamino)methyl]naphthalen-2-ol (**1a**) and enaminonitrile **2d** in Ac_2O: the resulting cycloadduct **C** eliminates a molecule of morpholine, and then Ac_2O adds at the C=C bond (Scheme 3). There are practically no examples in the literature of the addition of Ac_2O to the C=C bond in the absence of a catalyst.[8] The gas chromato-mass spectrometry data of the reaction product of compounds **1a** and **2d** indicate the formation of benzochromane **7** in the form of a mixture of geometric isomers **7a**,**b** in about 1:1 ratio, which indicates the low selectivity of the attack by the acetate anion on the cationic intermediate **D** from opposite sides. It was not possible to preparatively separate the isomer mixture.

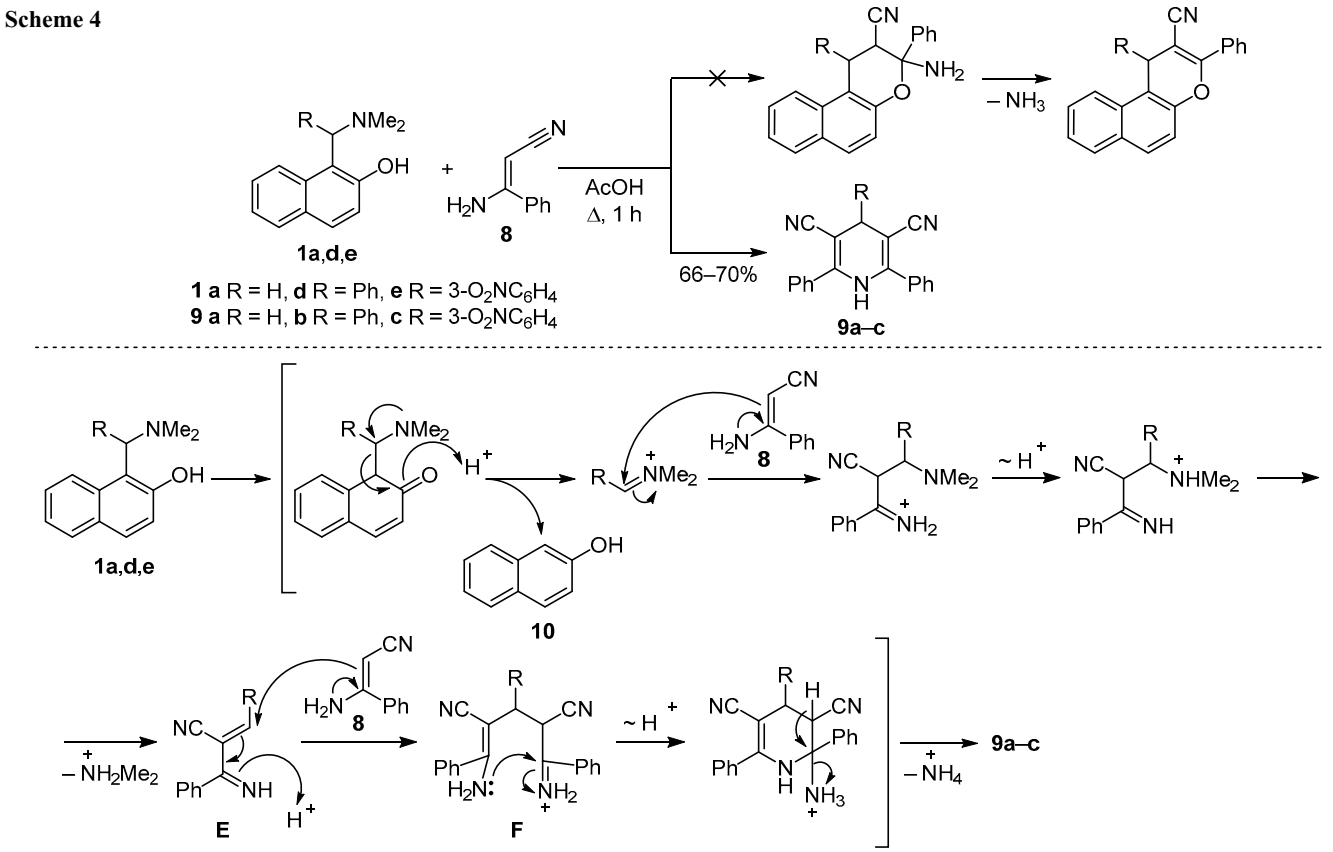
The IR spectrum of 2-acetyl-2-cyano-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl acetate (**7**) contains an intense absorption band of the CN group at 2222 cm^{-1} and absorption bands of the C=O groups at 1789 and 1751 cm^{-1}. ^{1}H and ^{13}C NMR spectra of isomers **7a**,**b** are identical. The protons 1-CH_2 and 3-CH appear as doublets at 3.97 and 7.84 ppm, respectively ($^4J_{H(1)–H(3)}$ = 1.4 Hz). In the ^{13}C NMR spectrum, the C-1 carbon atom resonates at 23.4 ppm, the signals of the carbon atoms of the C=O groups appear at 165.5 and 169.5 ppm. The mass spectra of isomers **7a**,**b** are also almost identical and contain the molecular ion (*m*/*z* 309) and a number of fragmentation ions characteristic of the benzochromane fragment. The gas chromatogram contains two peaks with different retention times (13.25 and 13.32 min).

Upon heating 3-amino-3-phenylacrylonitrile (**8**) with naphthalen-2-ol derivatives **1a**,**d**,**e**, 1,4-dihydropyridines **9a**–**c** are formed instead of benzochromanes or benzochromenes. Apparently, Mannich base **1a**,**d**,**e** undergoes the retro-Mannich reaction, leading to naphthalen-2-ol (**10**), which can be detected in the reaction mixture, and the iminium cation. The iminium cation adds to the conjugated system of enaminonitrile **8** with the formation of intermediate **E**, which then reacts with another molecule of the push-pull olefin **8**, forming the protonated form of dicyanodiene diamine **F**. Subsequent heterocyclization and deamination lead to 1,4-dihydropyridines **9a**–**c** (Scheme 4). A similar

Scheme 3



Scheme 4



route is described in the literature for the synthesis of 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarbonitriles from 3-amino-3-phenylacrylonitrile in comparable yields, including the use of different aldehydes as electrophiles.[9] Conducting the reaction in boiling DMF leads to a complex mixture of unidentifiable products.

The IR spectra of 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarbonitriles **9a**–**c** contain absorption bands of the N–H bond in the region of 3213–3298 cm^{-1} and of the C≡N bonds in the 2198–2206 cm^{-1} region. In the ^{13}C NMR spectra, the carbon atoms of the CN groups resonate at 119.1–120.0 ppm, and the signals of the C-3,5 carbon atoms associated with them appear in the 79.8–83.9 ppm range.

To conclude, we have shown that *N*,*N*-disubstituted β-enaminonitriles and esters act as dienophiles in reactions with 1,2-naphthoquinone 1-methide precursors, which leads to the formation of benzochromane derivatives.

Experimental

IR spectra were registered on a Shimadzu IR Affinity-1 spectrometer with a Specac Diamond ATR GS10800-B attachment. ^1H, ^{13}C NMR spectra (400 and 100 MHz, respectively), as well as COSY, ^1H–^{13}C HMBC, ^1H–^{13}C HMQC spectra (compound **7**) and DEPT experiments were acquired on a JEOL JNM-ECX400 spectrometer in DMSO-d_6 (compounds **4b**–**d**, **6a**,**c**, and **9b**,**c**) or $CDCl_3$ (compounds **3a**–**e**, **4a**, **6b**, **7**, and **9a**), using the residual solvent signals (DMSO-d_6: 2.50 ppm for ^1H, 39.5 ppm for ^{13}C nuclei; $CHCl_3$: 7.26 ppm for ^1H, 77.2 ppm for ^{13}C nuclei) as internal standard. Mass spectra were recorded on

a Finnigan Trace DSQ GC-MS system (EI ionization, 70 eV; BPX-5MS column (0.32 mm × 30 m, stationary phase thickness 0.25 μm); temperature program: 1 min at 80°C, ramp to 350°C at 20°C/min rate, 5 min at 350°C; carrier gas helium, 1.5 ml/min flow). Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer. Melting points were determined by the capillary method on an SRS OptiMelt MPA100 apparatus. Merck Silica gel 60, 0.04–0.063 mm, was used for column chromatography. TLC was performed on Merck Silica gel 60 F_{254} plates, eluent CH_2Cl_2, visualization under UV light or in I_2 vapor.

Mannich bases **1a**–**e**,[10] push-pull β-aminoacrylonitriles **2a**–**e**,[11] acrylate **5**,[12] and nitrile **8**[13] were obtained by known methods.

Synthesis of 2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles 3a–e and 2-[(2-hydroxynaphthalen-1-yl)methyl]-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles 4a–d (General procedure). Method I. A mixture of β-aminoacrylonitrile **2a**–**e** (1.5 mmol) and Mannich base **1a** (300 mg, 1.5 mmol) in DMF (10 ml) was heated under reflux for 1 h. DMF was evaporated under reduced pressure, and the residue was separated by column chromatography (SiO_2, eluent $CHCl_3$–EtOH, 15:1), followed by recrystallization from EtOH (compounds **3a**–**e**) or EtOH–DMF, 5:1 (compounds **4a**–**d**).

Method II. A mixture of β-aminoacrylonitrile **2a**–**c** (1.5 mmol) and Mannich base **1a** (600 mg, 3.0 mmol) in DMF (15 ml) was heated under reflux for 1 h. Isolation and purification of products was carried out similarly to method I.

Method III. A solution of Mannich base **1a** (300 mg, 1.5 mmol) in DMF (5 ml) was added dropwise with stirring to a solution of β-aminoacrylonitrile **2a**–**d** (1.5 mmol) in DMF (10 ml) at 150°C over 30 min. DMF was evaporated under reduced pressure, the residue was dissolved in EtOH (10 ml), and the mixture was kept at –20°C for 24 h. The precipitate was filtered off and recrystallized from EtOH.

Method IV. A mixture of nitrile **3b** (280 mg, 1.0 mmol) and Mannich base **1a** (200 mg, 1.0 mmol) in DMF (10 ml) was heated under reflux for 12 h. DMF was evaporated under reduced pressure, and the residue was recrystallized from EtOH.

Method V. A mixture of nitrile **3b**–**d** (1.0 mmol), Mannich base **1a** (200 mg, 1.0 mmol), and piperidine (0.1 ml, 1 mmol) in DMF (10 ml) was heated under reflux for 1 h. Isolation and purification of the product was carried out similarly to method IV.

***trans*-3-(Diethylamino)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (3a)**. Yield 172 mg (41%, method I), 100 mg (24%, method II), 303 mg (72%, method III), colorless crystals, mp 106–108°C. IR spectrum, ν, cm^{-1}: 2251 (CN), 1626, 1601, 1516, 1435, 1406, 1398, 1358, 1294, 1275, 1231, 1190, 1109, 1076, 1020, 955, 935, 860, 812, 802, 770, 746. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 (6H, t, *J* = 7.2, $2C\underline{H}_3CH_2$); 3.15–3.30 (2H, m, 1-CH_2); 3.40 (4H, q, *J* = 7.2, $2CH_3C\underline{H}_2$); 3.58–3.72 (1H, m, 2-CH); 5.01 (1H, d, *J* = 9.2, 3-CH); 7.10 (1H, d, *J* = 8.8, H Ar); 7.41–7.45 (1H, m, H Ar); 7.50–7.54 (1H, m, H Ar); 7.65 (1H, d, *J* = 9.1, H Ar); 7.71–7.76 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 13.0 ($2CH_3$); 27.4 (C-1); 29.3 (C-2); 52.3 ($2CH_3\underline{C}H_2$); 86.1 (C-3); 111.6; 119.5 (CH); 119.9 (CN); 120.2 (CH); 123.6 (CH); 126.5 (CH); 128.8 (CH); 129.4 (CH); 129.8; 131.0; 152.1 (C-4a). Found, %: C 77.20; H 7.26; N 9.88. $C_{18}H_{20}N_2O$. Calculated, %: C 77.11; H 7.19; N 9.99.

***trans*-3-(Pyrrolidin-1-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (3b)**. Yield 179 mg (43%, method I), 122 mg (29%, method II), 335 mg (80%, method III), colorless crystals, mp 123–125°C. IR spectrum, ν, cm^{-1}: 2245 (CN), 1620, 1601, 1510, 1468, 1406, 1246, 1180, 1115, 1020, 932, 816, 741. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.52–1.60 (4H, m, $2CH_2$); 3.18–3.22 (4H, m, $2CH_2N$); 3.25–3.34 (2H, m, 1-CH_2); 3.61–3.71 (1H, m, 2-CH); 4.86 (1H, d, *J* = 9.2, 3-CH); 7.14 (1H, d, *J* = 8.8, H Ar); 7.41–7.45 (1H, m, H Ar); 7.55–7.60 (1H, m, H Ar); 7.64 (1H, d, *J* = 8.4, H Ar); 7.74–7.79 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 22.5 ($2CH_2$); 27.9 (C-1); 29.3 (C-2); 51.4 ($2CH_2N$); 88.9 (C-3); 111.3; 118.9 (CH); 119.8 (CN); 120.6 (CH); 123.1 (CH); 127.2 (CH); 128.8 (CH); 129.8 (CH); 129.9; 131.5; 153.4 (C-4a). Found, %: C 77.59; H 6.59; N 9.93. $C_{18}H_{18}N_2O$. Calculated, %: C 77.67; H 6.52; N 10.06.

***trans*-3-(Piperidin-1-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (3c)**. Yield 202 mg (46%, method I), 131 mg (30%, method II), 364 mg (83%, method III), colorless crystals, mp 149–151°C. IR spectrum, ν, cm^{-1}: 2247 (CN), 1622, 1601, 1584, 1514, 1491, 1460, 1433, 1404, 1290, 1250, 1186, 1155, 1117, 1069, 1018, 945, 868, 822, 754. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20–2.23 (2H, m, $CH_2C\underline{H}_2CH_2$); 2.35–2.38 (4H, m, $C\underline{H}_2CH_2C\underline{H}_2$); 3.30–3.47 (2H, m, 1-$CH_2$); 3.60–3.65 (1H, m, 2-CH); 3.78–3.82 (4H, m, $2CH_2N$); 4.72 (1H, d, *J* = 9.2, 3-CH); 7.02 (1H, d, *J* = 8.8, H Ar); 7.35–7.39 (1H, m, H Ar); 7.49–7.54 (1H, m, H Ar); 7.66 (1H, d, *J* = 8.8, H Ar); 7.70 (1H, d, *J* = 8.4, H Ar); 7.76 (1H, d, *J* = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 25.3 ($CH_2\underline{C}H_2CH_2$); 26.8 ($\underline{C}H_2CH_2\underline{C}H_2$); 27.9 (C-1); 28.7 (C-2); 55.8 ($2CH_2N$); 86.5 (C-3); 111.0; 118.9 (CH); 119.5 (CN); 121.4 (CH); 124.0 (CH); 127.2 (CH); 129.1 (CH); 129.4 (CH); 130.0; 132.4; 151.2 (C-4a). Found, %: C 78.10; H 6.99; N 9.43. $C_{19}H_{20}N_2O$. Calculated, %: C 78.05; H 6.90; N 9.58.

***trans*-3-(Morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (3d)**. Yield 230 mg (52%, method I), 371 mg (84%, method III), colorless crystals, mp 152–154°C. IR spectrum, ν, cm^{-1}: 2241 (CN), 1622, 1599, 1404, 1275, 1231, 1190, 1118, 1069, 1022, 935, 860, 822, 812, 800, 768, 744. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.84–2.91 (2H, m, CH_2N); 3.03–3.09 (2H, m, CH_2N); 3.32–3.52 (2H, m, 1-CH_2); 3.62–3.67 (1H, m, 2-CH); 3.77–3.86 (4H, m, $2CH_2O$); 4.74 (1H, d, *J* = 9.2, 3-CH); 7.05 (1H, d, *J* = 9.0, H Ar); 7.37–7.41 (1H, m, H Ar); 7.50–7.55 (1H, m, H Ar); 7.67 (1H, d, *J* = 8.9, H Ar); 7.71 (1H, d, *J* = 8.2, H Ar); 7.78 (1H, d, *J* = 7.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.8 (C-1); 28.7 (C-2); 47.8 ($2CH_2N$); 67.0 ($2CH_2O$); 91.0 (C-3); 110.0; 118.6 (CH); 119.2 (CN); 121.7 (CH); 124.2 (CH); 127.2 (CH); 128.7 (CH); 129.2 (CH); 129.3; 132.0; 151.8 (C-4a). Found, %: C 73.38; H 6.08; N 9.40. $C_{18}H_{18}N_2O_2$. Calculated, %: C 73.45; H 6.16; N 9.52.

***trans*-3-(Diphenylamino)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (3e)**. Yield 440 mg (78%, method I),

colorless crystals, mp 225–227°C. IR spectrum, ν, cm^{-1}: 2247 (CN), 1624, 1591, 1499, 1468, 1398, 1256, 1215, 1182, 1138, 1074, 955, 816, 762, 745, 700, 685. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.13 (1H, ddd, *J* = 11.7, *J* = 9.8, *J* = 6.4, 2-CH); 3.50 (1H, dd, *J* = 16.5, *J* = 11.7) and 3.60 (1H, dd, *J* = 16.5, *J* = 6.4, 1-CH_2); 6.01 (1H, d, *J* = 9.8, 3-CH); 7.13–7.19 (3H, m, H Ar); 7.31–7.43 (9H, m, H Ar); 7.51–7.56 (1H, m, H Ar); 7.70 (2H, d, *J* = 8.7, H Ar); 7.79 (1H, d, *J* = 7.6, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.7 (C-1); 30.0 (C-2); 85.3 (C-3); 109.8; 118.8 (CH); 119.2 (CN); 121.7 (CH); 124.3 (CH); 124.7 (2CH); 124.8 (4CH); 127.3 (CH); 128.7 (CH); 129.2 (CH); 129.3; 129.5 (4CH); 131.9; 145.2 (2C-1 Ph); 151.4 (C-4a). Found, %: C 82.90; H 5.30; N 7.32. $C_{26}H_{20}N_2O$. Calculated, %: C 82.95; H 5.36; N 7.44.

(2*R,3*R**)-3-(Diethylamino)-2-[(2-hydroxynaphthalen-1-yl)methyl]-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (4a)**. Yield 118 mg (18%, method I), 354 mg (54%, method II), colorless crystals, mp 223–225°C. IR spectrum, ν, cm^{-1}: 3400–3100 (OH), 2232 (CN), 1620, 1597, 1510, 1468, 1450, 1408, 1281, 1234, 1215, 1180, 1134, 1094, 1020, 997, 968, 860, 825, 810, 772, 764, 756, 748. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15–1.18 (6H, m, 2C$\underline{H}_3$CH_2); 1.87 (2H, br. s, CH_3C$\underline{H}_2$); 1.95 (2H, br. s, CH_3C$\underline{H}_2$); 3.13 (1H, d, *J* = 16.5) and 3.68 (1H, d, *J* = 16.5, 1-CH_2); 3.75 (1H, d, *J* = 15.4) and 3.98 (1H, d, *J* = 15.4, CH_2Ar); 4.29 (1H, s, 3-CH); 7.07 (1H, d, *J* = 8.7, H Ar); 7.18 (1H, d, *J* = 8.7, H Ar); 7.29–7.44 (4H, m, H Ar); 7.62 (1H, d, *J* = 8.7, H Ar); 7.69–7.75 (3H, m, H Ar); 7.80 (1H, d, *J* = 8.0, H Ar); 8.09 (1H, d, *J* = 8.4, H Ar); 11.22 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 23.8 ($2CH_3$); 29.6 (CH_2); 35.5 (CH_2); 39.8 (C-2); 46.9 ($2CH_3\underline{C}H_2$); 92.2 (C-3); 110.5; 110.8; 118.1 (CH); 120.2 (CH); 121.6 (CH); 122.1; 122.8 (CH); 123.1 (CH); 124.1 (CH); 126.9 (CH); 127.0 (CH); 128.7 (CH); 129.1 (2CH); 129.2; 129.5; 130.6 (CH); 132.3; 135.0; 151.2 (C-4a); 155.5 (C–OH). Found, %: C 79.85; H 6.55; N 6.33. $C_{29}H_{28}N_2O_2$. Calculated, %: C 79.79; H 6.47; N 6.42.

(2*R,3*R**)-2-[(2-Hydroxynaphthalen-1-yl)methyl]-3-(pyrrolidin-3-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (4b)**. Yield 110 mg (17%, method I), 331 mg (51%, method II), 100 mg (23%, method IV), 352 mg (81%, method V), colorless crystals, mp 229–231°C. IR spectrum, ν, cm^{-1}: 3200–3000 (OH), 2234 (CN), 1622, 1597, 1468, 1402, 1285, 1225, 1209, 1180, 1157, 1084, 995, 951, 864, 824, 810, 772, 754, 746. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.83 (4H, br. s, $2CH_2$); 3.15–3.23 (4H, m, $2CH_2$N); 3.29 (1H, d, *J* = 16.7, 1-CH_A); 3.44 (1H, d, *J* = 14.2, CH_AAr); 3.64 (1H, d, *J* = 16.7, 1-CH_B); 3.88 (1H, d, *J* = 14.2, CH_BAr); 5.26 (1H, s, 3-CH); 7.09 (1H, d, *J* = 8.9, H Ar); 7.24–7.35 (3H, m, H Ar); 7.43–7.50 (3H, m, H Ar); 7.70 (1H, d, *J* = 8.9, H Ar); 7.75 (1H, d, *J* = 8.9, H Ar); 7.78–7.81 (2H, m, H Ar); 8.21 (1H, d, *J* = 8.5, H Ar); 10.17 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 24.7 ($2CH_2$); 29.2 (CH_2); 35.6 (CH_2); 40.9 (C-2); 47.6 ($2CH_2$N); 91.2 (C-3); 111.3; 113.8; 118.7 (CH); 118.9 (CH); 121.7 (CH); 121.8; 123.0 (CH); 124.1 (2CH); 126.5 (CH); 127.4 (CH); 128.8; 128.9 (CH); 129.0 (2CH); 129.1; 129.6 (CH); 132.4; 134.7; 152.1 (C-4a); 154.9 (C–OH). Found, %: C 80.05; H 6.11; N 6.32. $C_{29}H_{26}N_2O_2$. Calculated, %: C 80.16; H 6.03; N 6.45.

(2*R,3*R**)-2-[(2-Hydroxynaphthalen-1-yl)methyl]-3-(piperidin-1-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (4c)**. Yield 102 mg (15%, method I), 322 mg (48%, method II), 346 mg (77%, method V), colorless crystals, mp 235–237°C. IR spectrum, ν, cm^{-1}: 3200–3000 (OH), 2234 (CN), 1620, 1597, 1468, 1408, 1281, 1215, 1180, 1161, 1134, 1094, 1082, 997, 968, 824, 810, 746. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.51–1.55 (2H, m, $CH_2C\underline{H}_2CH_2$); 1.64–1.69 (4H, m, $C\underline{H}_2CH_2C\underline{H}_2$); 2.84–2.87 (4H, m, $2CH_2$N); 3.22 (1H, d, *J* = 16.7, 1-CH_A); 3.39 (1H, d, *J* = 14.2, CH_AAr); 3.69 (1H, d, *J* = 16.7, 1-CH_B); 3.92 (1H, d, *J* = 14.2, CH_BAr); 5.00 (1H, s, 3-CH); 7.10 (1H, d, *J* = 8.9, H Ar); 7.25–7.34 (3H, m, H Ar); 7.37–7.52 (3H, m, H Ar); 7.71 (1H, d, *J* = 9.0, H Ar); 7.76 (1H, d, *J* = 8.9, H Ar); 7.79–7.82 (2H, m, H Ar); 8.18 (1H, d, *J* = 8.7, H Ar); 10.15 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 24.6 ($CH_2\underline{C}H_2CH_2$); 26.2 ($\underline{C}H_2CH_2\underline{C}H_2$); 28.8 ($CH_2$); 36.5 ($CH_2$); 39.2 (C-2); 52.8 ($2CH_2$N); 95.4 (C-3); 111.4; 113.8; 118.7 (CH); 118.9 (CH); 121.6 (CH); 122.1; 123.0 (CH); 124.0 (CH); 124.2 (CH); 126.6 (CH); 127.5 (CH); 128.8; 129.0 (2CH); 129.1 (CH, C Ar); 129.6 (CH); 132.4; 134.7; 152.3 (C-4a); 154.8 (C–OH). Found, %: C 80.36; H 6.33; N 6.14. $C_{30}H_{28}N_2O_2$. Calculated, %: C 80.33; H 6.29; N 6.25.

(2*R,3*R**)-2-[(2-Hydroxynaphthalen-1-yl)methyl]-3-(morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carbonitrile (4d)**. Yield 108 mg (16%, method I), 325 mg (48%, method II), 335 mg (74%, method V), colorless crystals, mp 238–240°C. IR spectrum, ν, cm^{-1}: 3400–3000 (OH), 2941, 2862, 2236 (CN), 1620, 1599, 1510, 1468, 1400, 1285, 1225, 1157, 993, 864, 812, 771, 754, 746. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.22–3.29 (5H, m, $2CH_2$N, 1-CH_A); 3.42 (1H, d, *J* = 14.4, CH_AAr); 3.61 (1H, d, *J* = 16.4, 1-CH_B); 3.85 (1H, d, *J* = 14.4, CH_BAr); 3.91–3.94 (4H, m, $2CH_2$O); 5.23 (1H, s, 3-CH); 7.06 (1H, d, *J* = 8.8, H Ar); 7.22–7.32 (3H, m, H Ar); 7.41–7.48 (3H, m, H Ar); 7.68 (1H, d, *J* = 8.8, H Ar); 7.73 (1H, d, *J* = 8.8, H Ar); 7.75–7.79 (2H, m, H Ar); 8.16 (1H, d, *J* = 8.4, H Ar); 10.15 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 30.4 (CH_2); 36.8 (CH_2); 40.9 (C-2); 48.8 ($2CH_2$N); 67.6 ($2CH_2$O); 92.3 (C-3); 112.4; 115.0; 119.9 (CH); 120.1 (CH); 122.8 (CH); 122.9; 124.2 (CH); 125.3 (2CH); 127.0 (CH); 128.6 (CH); 130.0; 130.1 (CH); 130.2 (2CH); 130.3 (CH); 131.2; 133.6; 135.9; 153.6 (C-4a); 155.9 (C–OH). Found, %: C 77.38; H 5.87; N 6.20. $C_{29}H_{26}N_2O_3$. Calculated, %: C 77.31; H 5.82; N 6.22.

Synthesis of methyl *trans*-3-(morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carboxylates 6a–c (General method). A mixture of methyl 3-morpholinoacrylate (**5**) (260 mg, 1.5 mmol) and Mannich base **1a**–**c** (1.5 mmol) in DMF (5 ml) was heated under reflux for 3 h. DMF was evaporated under reduced pressure, and the residue was recrystallized twice from EtOH.

Methyl *trans*-3-(morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carboxylate (6a). Yield 360 mg (73%), colorless crystals, mp 179–181°C. IR spectrum, ν, cm^{-1}: 2845, 1732 (C=O), 1624, 1599, 1433, 1400, 1290, 1263, 1029, 1159, 1117, 953, 808, 764. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65–2.72 (2H, m, CH_2N); 2.96–3.03 (2H, m, CH_2N); 3.17–3.26 (2H, m, 1-CH_2); 3.32–3.42 (1H, m, 2-CH); 3.49–3.61 (4H, m, $2CH_2$O); 3.70 (3H, s, CH_3); 4.68 (1H, d, *J* = 9.2, 3-CH); 7.03 (1H, d, *J* = 8.9, H Ar); 7.31–

7.36 (1H, m, H Ar); 7.45–7.50 (1H, m, H Ar); 7.68 (1H, d, *J* = 8.9, H Ar); 7.77–7.81 (2H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 26.3 (C-1); 40.9 (C-2); 48.1 ($2CH_2N$); 52.4 (CH_3); 67.1 ($2CH_2O$); 92.6 (C-3); 112.5; 119.0 (CH); 122.6 (CH); 124.0 (CH); 127.2 (CH); 128.5 (CH); 128.8 (CH); 129.1; 132.7; 151.9 (C-4a); 173.0 (C=O). Found, %: C 69.79; H 6.44; N 4.15. $C_{19}H_{21}NO_4$. Calculated, %: C 69.71; H 6.47; N 4.28.

Methyl *trans*-8-bromo-3-(morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carboxylate (6b). Yield 470 mg (77%), colorless crystals, mp 243–245°C. IR spectrum, ν, cm^{-1}: 1734 (C=O), 1603, 1489, 1443, 1391, 1236, 1190, 1115, 978, 885, 822, 750, 702. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.85–2.89 (2H, m, CH_2N); 3.04–3.07 (2H, m, CH_2N); 3.29–3.44 (2H, m, 1-CH_2); 3.59–3.64 (1H, m, 2-CH); 3.78–3.87 (4H, m, $2CH_2O$); 3.95 (3H, s, CH_3); 4.72 (1H, d, *J* = 9.2, 3-CH); 7.20 (1H, d, *J* = 8.8, H Ar); 7.63 (1H, d, *J* = 8.8, H Ar); 7.65–7.70 (2H, m, H Ar); 7.97 (1H, s, H-7). ^{13}C NMR spectrum, δ, ppm: 27.8 (C-1); 41.3 (C-2); 47.7 ($2CH_2N$); 52.8 (CH_3); 67.1 ($2CH_2O$); 90.9 (C-3); 110.0; 116.6; 118.7; 121.7 (CH); 124.2 (CH); 127.2 (CH); 128.7 (CH); 129.2 (CH); 132.0; 152.8 (C-4a); 175.6 (C=O). Found, %: C 56.24; H 5.04; N 3.49. $C_{19}H_{20}BrNO_4$. Calculated, %: C 56.17; H 4.96; N 3.45.

Methyl *trans*-8-(adamantan-1-yl)-3-(morpholin-4-yl)-2,3-dihydro-1*H*-benzo[*f*]chromene-2-carboxylate (6c). Yield 560 mg (81%), colorless crystals, mp 293–295°C. IR spectrum, ν, cm^{-1}: 2895 (CH Ad), 2847 (CH Ad), 1732 (C=O), 1603, 1439, 1396, 1263, 1236, 1204, 1190, 1161, 1121, 980, 810. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.59–1.68 (6H, m, $3CH_2$ Ad); 1.93 (6H, br. s, $3CH_2$ Ad); 1.99 (3H, br. s, 3CH Ad); 2.63–2.68 (2H, m, CH_2N); 2.82–2.88 (2H, m, CH_2N); 3.26–3.34 (2H, m, 1-CH_2); 3.40–3.51 (1H, m, 2-CH); 3.84–3.92 (4H, m, $2CH_2O$); 3.97 (3H, s, CH_3); 4.72 (1H, d, *J* = 9.2, 3-CH); 7.03 (1H, d, *J* = 8.8, H Ar); 7.36–7.39 (1H, m, H Ar); 7.49–7.51 (1H, m, H Ar); 7.65 (1H, d, *J* = 8.8, H Ar); 7.69 (1H, d, *J* = 8.4, H Ar). ^{13}C NMR spectrum, δ, ppm: 26.4 (C-1); 28.3 (3CH Ad); 35.9 ($3CH_2$ Ad); 39.5 ($3CH_2$ Ad); 41.1 (C Ad); 42.0 (C-2); 48.3 ($2CH_2N$); 52.6 (CH_3); 66.9 ($2CH_2O$); 93.6 (C-3); 112.0; 117.8 (CH); 123.4 (CH); 125.4 (CH); 127.6; 128.8 (CH); 129.3 (CH); 130.0; 131.7; 152.4 (C-4a); 172.9 (C=O). Found, %: C 75.51; H 7.69; N 3.12. $C_{29}H_{35}NO_4$. Calculated, %: C 75.46; H 7.64; N 3.03.

2-Acetyl-2-cyano-2,3-dihydro-1*H*-benzo[*f*]chromen-3-yl acetate (7), a mixture of geometric isomers **7a**,**b** in a 1:1 ratio. A solution of β-enaminonitrile **2d** (210 mg, 1.5 mmol) and Mannich base **1a** (310 mg, 1.5 mmol) in Ac_2O (5 ml) was heated under reflux for 10 h. The mixture was cooled to –20°C, the formed precipitate was filtered off and washed with EtOH (1 ml). The product was recrystallized from EtOAc. Yield 222 mg (48%), colorless crystals, mp 115–120°C. IR spectrum, ν, cm^{-1}: 2222 (CN), 1789 (C=O), 1751 (C=O), 1643, 1438, 1373, 1203, 1165, 1134, 1064, 910, 767. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15 (3H, s, CH_3); 2.42 (3H, s, CH_3); 3.97 (2H, d, *J* = 1.4, 1-CH_2); 7.27 (1H, d, *J* = 8.9, H-5); 7.48 (1H, ddd, *J* = 8.2, *J* = 7.1, *J* = 1.4, H-8); 7.54 (1H, ddd, *J* = 8.2, *J* = 7.1, *J* = 1.4, H-9); 7.82 (1H, d, *J* = 8.5, H-6); 7.84 (1H, d, *J* = 1.4, 3-CH); 7.87 (1H, dd, *J* = 7.6, *J* = 1.4, H-7); 7.96 (1H, d, *J* = 8.5, H-10). ^{13}C NMR spectrum, δ, ppm: 20.4 (CH_3); 21.3 (CH_3); 23.4 (C-1); 98.9 (C-2); 117.6 (CN); 121.7 (C-5); 122.4 (C-10b); 123.5 (C-10); 125.7 (C-8); 127.0 (C-9); 129.1 (C-7); 129.4 (C-6); 132.0 (C-6a); 132.5 (C-10a); 146.2 (C-3); 147.4 (C-4a); 165.5 (C=O); 169.5 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 309 $[M]^+$ (5), 268 $[M–CH_2=C=O]^+$ (30), 226 $[M–2CH_2=C=O]^+$ (95), 225 $[M–CH_2=C=O, –CH_3CO]^+$ (80), 196 (42), 180 (22), 169 (24), 168 (34), 157 (65), 144 (90), 139 (52), 128 (65), 115 (48), 43 $[CH_3CO]^+$ (100). Found, %: C 69.82; H 4.98; N 4.42. $C_{18}H_{15}NO_4$. Calculated, %: C 69.89; H 4.89; N 4.53.

Synthesis of 2,6-diphenyl-1,4-dihydropyridine-3,5-dicarbonitriles 9a–c (General method). A mixture of 3-amino-3-phenylacrylonitrile (**8**) (150 mg, 1.0 mmol) and Mannich base **1a**,**d**,**e** (1.0 mmol) in AcOH (3 ml) was heated under reflux for 1 h. The solution was cooled to room temperature, the precipitate was filtered off, washed with ice-cold MeOH (1 ml), and air-dried at room temperature.

2,6-Diphenyl-1,4-dihydropyridine-3,5-dicarbonitrile (9a). Yield 187 mg (66%), colorless crystals, mp 226–227°C (mp 228–229°C (AcOH)[9]). IR spectrum, ν, cm^{-1}: 3298 (NH), 3055, 2927, 2893, 2198 (CN), 1627 (C=C), 1477, 1276, 767. ^{1}H NMR spectrum, δ, ppm: 3.57 (2H, s, 4-CH_2); 6.07 (1H, br. s, NH); 7.46–7.52 (6H, m, H Ph); 7.54–7.58 (4H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 27.8 (C-4); 79.8 (C-3,5); 119.1 (2CN); 127.4 (4CH); 129.5 (4CH); 131.5 (2CH); 132.7 (2C); 149.4 (C-2,6). Found, %: C 80.60; H 4.65; N 14.72. $C_{19}H_{13}N_3$. Calculated, %: C 80.54; H 4.62; N 14.83.

2,4,6-Triphenyl-1,4-dihydropyridine-3,5-dicarbonitrile (9b). Yield 250 mg (70%), colorless crystals, mp 305–307°C (mp 305–306°C (AcOH)[9]). IR spectrum, ν, cm^{-1}: 3213 (NH), 3097, 2962, 2777, 2198 (CN), 1639 (C=C), 1496, 1284, 694. ^{1}H NMR spectrum, δ, ppm: 4.67 (1H, s, 4-CH); 7.45–7.51 (10H, m, H Ph); 7.58–7.63 (5H, m, H Ph); 10.12 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 42.9 (C-4); 83.9 (C-3,5); 120.0 (2CN); 128.1 (2CH); 128.5 (CH); 129.0 (4CH); 129.3 (4CH); 129.7 (2CH); 131.3 (2CH); 132.8 (2C); 144.5 (C Ph); 149.6 (C-2,6). Found, %: C 83.48; H 4.70; N 11.50. $C_{25}H_{17}N_3$. Calculated, %: C 83.54; H 4.77; N 11.69.

4-(3-Nitrophenyl)-2,6-diphenyl-1,4-dihydropyridine-3,5-dicarbonitrile (9c). Yield 275 mg (68%), colorless crystals, mp 275–278°C. IR spectrum, ν, cm^{-1}: 3217 (NH), 3097, 2924, 2777, 2206 (CN), 1639 (C=C), 1527 (NO_2), 1496, 1346 (NO_2), 1284, 1182, 836, 690. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.05 (1H, s, 4-CH); 7.46–7.54 (6H, m, H Ph); 7.61–7.64 (4H, m, H Ph); 7.78–7.83 (1H, m, H Ar); 7.99 (1H, d, *J* = 7.8, H Ar); 8.24 (1H, d, *J* = 8.2, H Ar); 8.29 (1H, s, H Ar); 10.29 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 42.1 (C-4); 83.0 (C-3,5); 119.7 (2CN); 122.6 (CH); 123.6 (CH); 129.0 (4CH); 129.3 (4CH); 131.5 (3CH); 132.6 (2C); 135.0 (CH); 146.3; 148.8; 150.3 (C-2,6). Found, %: C 74.30; H 3.94; N 13.79. $C_{25}H_{16}N_4O_2$. Calculated, %: C 74.25; H 3.99; N 13.85.

X-ray structural analysis of compounds 4b,c was performed on an STOE STADIVARI PILATUS 100K single crystal diffractometer (CuKα radiation, λ 1.5418 Å) at 295(2) K. Crystals were grown as colorless prisms from MeOH–CH_2Cl_2, 1:2 mixture by slow evaporation of the solvent at room temperature. Single crystals of compounds

4b,**c** with linear dimensions of 0.2 × 0.2 × 0.2 mm were selected for studies. Crystallographic data for compound **4b** ($C_{29}H_{26}N_2O_2$, *M* 434.52): crystals are triclinic, space symmetry group $P\bar{1}$; *a* 8.5164(5), *b* 11.5518(6), *c* 12.9967(8) Å; α 111.498(4), β 90.825(5), γ 107.522(4)°; *V* 1123.20(12) Å^3; *Z* 2; d_{calc} 1.285 g·cm^{-3}; μ 0.756 mm^{-1}; *F*(000) 460. Diffraction data were collected within 3.692° ≤ θ ≤ 72.857° range; sphere segment –10 ≤ *h* ≤ 10, –14 ≤ *k* ≤ 14, –16 ≤ *l* ≤ 10. 4020 independent reflections were collected, of which 1832 had $I > 2\sigma(I)$. The structure was solved by the direct methods and refined by the least squares technique in the full-matrix anisotropic approximation to R_1 0.0558 (wR_2 0.1218). The positions of all hydrogen atoms were calculated geometrically and refined according to the "rider" model.

Crystallographic data for compound **4c** ($C_{30}H_{28}N_2O_2$, *M* 448.54): crystals are triclinic, space symmetry group $P\bar{1}$; *a* 10.1409(9), *b* 10.8089(9), *c* 13.0232(11) Å; α 65.400(6), β 69.311(7), γ 65.190(7)°; *V* 1150.22(19) Å^3; *Z* 2; d_{calc} 1.295 g·cm^{-3}; μ 0.756 mm^{-1}; *F*(000) 476. Diffraction data were collected within 3.824° ≤ θ ≤ 72.856° range; sphere segment –12 ≤ *h* ≤ 10, –13 ≤ *k* ≤ 12, –14 ≤ *l* ≤ 16. 3874 independent reflections were collected, of which 1620 had $I > 2\sigma(I)$. The structure was solved by the direct methods and refined by the least squares technique in the full-matrix anisotropic approximation to R_1 0.0438 (wR_2 0.0750). The positions of all hydrogen atoms were calculated geometrically and refined according to the "rider" model.

The calculations were performed using the SHELXL software package.[14] The full set of X-ray structural data for compounds **4b**,**c** was deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1942274 and CCDC 1942630, respectively).

Supplementary information file containing ^{1}H and ^{13}C NMR spectra for compounds **3a**–**e**, **4a**–**d**, and **6a**–**c**, as well as COSY, ^{1}H–^{13}C HMBC, and ^{1}H–^{13}C HMQC spectra for compound **7**, is available at the journal website at http://link.springer.com/journal/10593.

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