One-step synthesis of substituted 2-amino-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans. Molecular and crystal structure of 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran

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Substituted 2-aminobenzo[*b*]pyrans were synthesized by three-component condensation of aromatic aldehydes, cyanoacetic acid derivatives, and cyclic 1,3-diketones. The molecular and crystal structure of 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran was established by X-ray diffraction analysis.

Key words: pyran, 1,3-cyclohexanedione, dimedone, benzopyran, X-ray diffraction analysis.

Substituted 2-amino-4*H*-benzo[*b*]pyrans attract attention because they can be used as drugs, immunomodulators,[1] and analogs of natural products[2] and other important compounds. In addition, 2-amino-4*H*-benzo[*b*]pyrans are used in the synthesis of difficultly accessible annelated heterocycles.[3]

Earlier,[4—7] benzannelated 2-amino-4*H*-pyrans **1** (Scheme 1) have been synthesized in two steps. The first step consists in preparing arylmethylenemalononitriles **2**. However, the synthesis and isolation of the latter are sometimes impossible[8] and are occasionally associated with a particular danger because these compounds are strong lacrimators and are similar in toxicity to the known war gas, *o*-chlorobenzylidenemalononitrile (CS).[9] The second step involves the reaction of the resulting unsaturated nitriles **2** with the corresponding diketones **3**. Earlier, 2-amino-3-cyano-4,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran has been synthesized without the preisolation of unsaturated nitrile.[10] We have also reported the one-step synthesis of substituted 2-amino-4*H*-benzo[*b*]pyrans.[11]

With the aim of simplifying these procedures and making them safe, in the present study we examined the possibility of the one-step synthesis of benzopyrans **1** without the preliminary synthesis of arylmethylenemalononitriles **2** by three-component condensation of aldehydes **4**, derivatives of cyanoacetic acid **5**, and cyclic 1,3-diketones **3a,b**, which we have developed earlier for the synthesis of spiro-4-(piperidino-4)-2*H*,4*H*-pyrano[2,3-*c*]pyrazoles.[12] The advantage of this method is that it is based on the simple one-step process in which the generation of product **1** (see Scheme 1) can take simultaneously two pathways (*A* and *B*), *viz.*, the reaction of unsaturated nitrile **2** with dicarbonyl compound **3** (path *A*) and the reaction of cyanoacetic acid derivative **5** with intermediate **6** (path *B*).

Under the same conditions, the reactions afforded many various 2-amino-4*H*-pyrans (see the Experimental section). For their synthesis, we used available aldehydes containing structural fragments of natural compounds and pharmaceuticals.[13] In addition to malononitrile, we used methyl, ethyl, isopropyl, *tert*-butyl, 2-methoxyethyl, and benzyl cyanoacetates as methylene-active nitriles. In none of the reactions under study, was transesterification observed in spite of the fact that the reactions were carried out in EtOH.

Earlier, 5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans have been synthesized with the use of cyclic 1,3-diketones.[4—7] In one study,[14] cyclohexanone (**7**) was proposed as a carbonyl compound for the synthesis of 4*H*-benzo[*b*]pyrans (Scheme 2). We repeated this experiment and found out that structure **8** has been erroneously assigned to the product with m.p. 247—250 °C, which has been prepared by refluxing a mixture of unsaturated nitrile **2** (Ar = Ph, Z = CN) and cyclohexanone (**7**) in EtOH in the presence of Et_3N as the catalyst.[14] In reality, the reactions performed under these conditions afforded substituted hexahydronaphthalenes **9**, which are generally synthesized by the reactions of unsaturated nitriles **2** with cyclohexylidenemalononitrile (**10**).[15]

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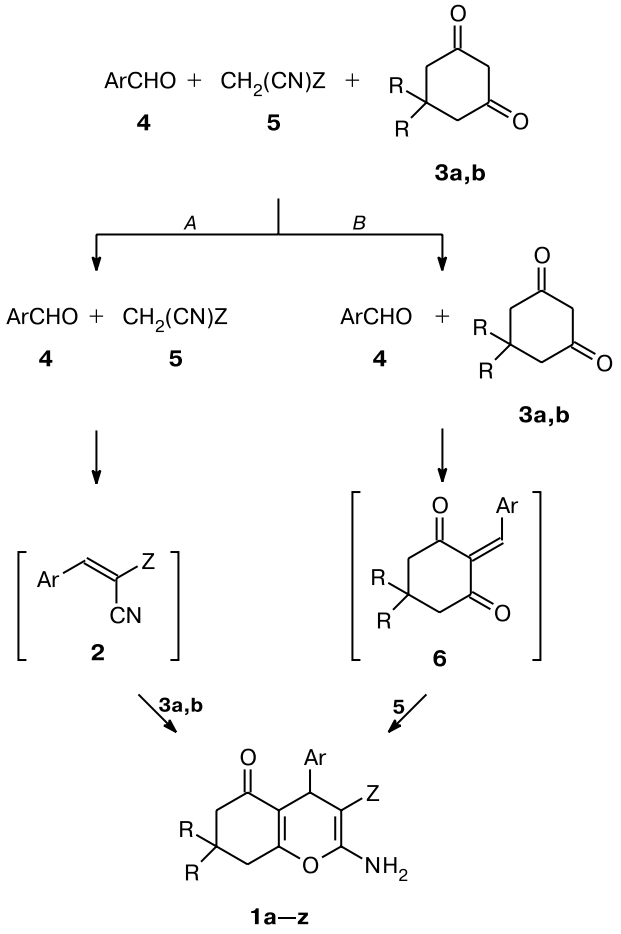
Scheme 1

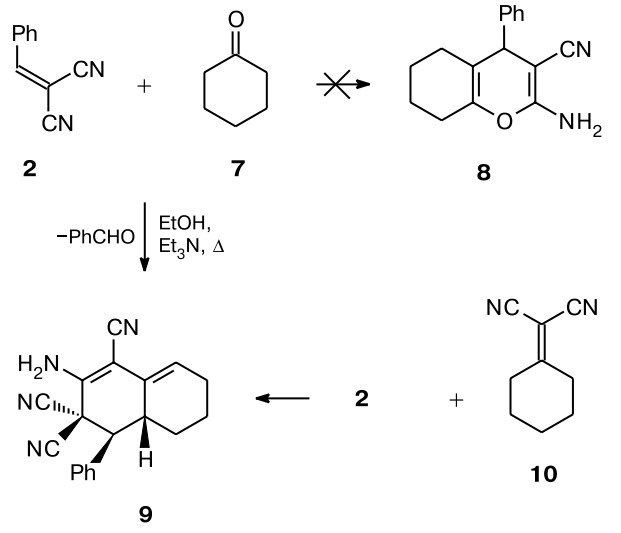


1: Ar = 4-OBu^n-3-OMeC$_6$H$_3$ (**a**), 5-Me-2-furyl (**b**), 4-ClC$_6$H$_4$ (**c**), 2-thienyl (**d**), 2,4-F$_2$C$_6$H$_3$ (**e, t**), 2-NO$_2$C$_6$H$_4$ (**f, j**), 3-NO$_2$C$_6$H$_4$ (**g, k, w**), 4-NO$_2$C$_6$H$_4$ (**h, l, x**), 4-pyridyl (**i, y**), 2,4,5-(OMe)$_3$-C$_6$H$_2$ (**m**), 4-OPr-3-OMeC$_6$H$_3$ (**n**), 3,4-(—OCH$_2$O—)-2-ClC$_6$H$_2$ (**o**), 4-(OCH$_2$C(O)NH$_2$)C$_6$H$_4$ (**p**), 4-(*N*-morpholinyl)-C$_6$H$_4$ (**q**), 4-(OCH$_2$CH$_2$-(*N*-morpholinyl))-3-OMeC$_6$H$_3$ (**r**), 2-FC$_6$H$_4$ (**s**), 4-COOMeC$_6$H$_4$ (**u, v, z**);
Z = CN (**a, b, j—r**), COOMe (**c, d, s**), COOEt (**e, t**), COOCH$_2$CH$_2$OMe (**f—i, w—y**), COOPr^i (**u**), COOBu^t (**v**), COOCH$_2$Ph (**z**)
R = H (**1a—i, 3a**), Me (**1j—z, 3b**)

We prepared 2-amino-4*H*-benzo[*b*]pyrans as stable analytically pure colorless powders, which can be recrystallized from EtOH or MeCN. The structures of all compounds were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis (see the Experimental section).

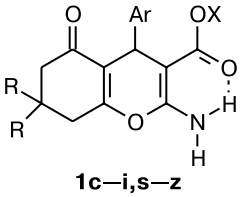
The IR spectra of the aminopyrans synthesized have a series of stretching absorption bands of the amino group (3455—3184 cm^{-1}) and an intense bending band of this group (1674—1650 cm^{-1}). The high intensity of the absorption band at 2204—2188 cm^{-1} confirms the presence of the cyano group conjugated with the amino group in

Scheme 2



pyrans **1a,b,j—r**. The absorption bands of the carbonyl groups are observed at 1704—1670 cm^{-1}.

The ^{1}H NMR spectra of compounds **1a—z** have characteristic signals for the protons of the amino group. Due to hydrogen bonding, these signals in the spectra of pyrans **1c—i,s—z** containing the carboxyl group at position 3 of the pyran ring are shifted downfield (δ 7.37—7.64) compared to those in the spectra of pyrans **1a,b,j—r** (δ 6.47—7.12)[16] containing the cyano group at position 3.



In the spectra of pyrans **1f—h,j—l**, the chemical shift δ of the signal for the proton of the C(4)H group sharply decreases (Table 1) as the position of the nitro group in the benzene ring changes from the *ortho* to *meta* and *para* positions. This is, apparently, attributable to an intramolecular contact between the H atom at C(4) and one of the O atoms of the nitro group in the *ortho* position of the phenyl substituent (C(4)H...O=N(O)C$_6$H$_4$). This con-

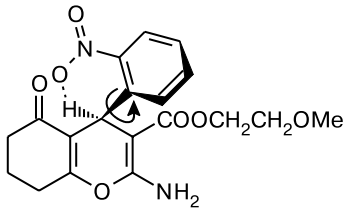
Table 1. Chemical shifts (δ) of the signals for the protons of the main fragments of 2-aminobenzo[*b*]pyrans **1f—h,j—l**

Compound	Position of NO_2 group	δ				
		C(4)H	C(6)H$_2$	C(7)H$_2$	C(8)H$_2$	NH$_2$
1f	*ortho*-	5.41	2.22	1.86	2.58	7.64
1g	*meta*-	4.68	2.29	1.93	2.66	7.61
1h	*para*-	4.67	2.29	1.92	2.65	7.61
1j	*ortho*-	4.96	2.11	—	2.50	7.06
1k	*meta*-	4.43	2.21	—	2.55	7.13
1l	*para*-	4.38	2.19	—	2.54	7.12

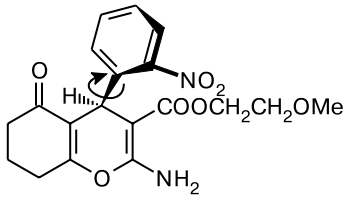
tact was detected by X-ray diffraction analysis. In addition, δ_H of all groups of the benzopyran ring in the spectra of pyrans **1f,j** containing the nitro group in the *ortho* position (and, presumably, having the C(4)H...O=N(O)C_6H_4 hydrogen bond) differ from those in the spectra of pyrans **1g,h,k,l** containing the nitro group in the *meta* or *para* positions.

According to the results of X-ray diffraction analysis of compound **1f**, the reaction afforded only the synperiplanar (*sp*) isomer of two possible isomers, *viz.*, the *sp* and antiperiplanar (*ap*) isomers. Earlier, we have observed the formation of only *sp* isomers for substituted 4-(2-nitrophenyl)-1,4-dihydropyridines,[17,18] 4-(2-nitrophenyl)-4*H*-thiopyrans,[19] and 4-(2-nitrophenyl)-4,5-dihydrothiophenes.[20] The *sp* isomers are, apparently, stabilized by an intramolecular contact C(4)H...O=N(O). This assumption is to some extent supported by the absence of atroposelectivity in the 2-amino-3-ethoxycarbonyl-4-(3-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran molecules, which exist (according to the X-ray diffraction data) as a mixture of the *sp* and *ap* isomers in a ratio of 2 : 1.[16]

The overall view of molecule **1f** is shown in Fig. 1. The bond lengths and bond angles are given in Tables 2 and 3, respectively. The atomic numbering scheme used in Fig. 1 differs from that assumed in the text.



1f (*sp* isomer)



1f (*ap* isomer)

The heterocycle in molecule **1f**, like those in the substituted 4*H*-pyrans studied earlier,[16,21,22] adopts a flattened boat conformation with the O(1) and C(4) atoms deviating from the plane (to within ±0.016 Å) passing through the remaining four atoms of the ring by 0.119 and 0.158 Å, respectively. The foldings along the O(1)...C(4),

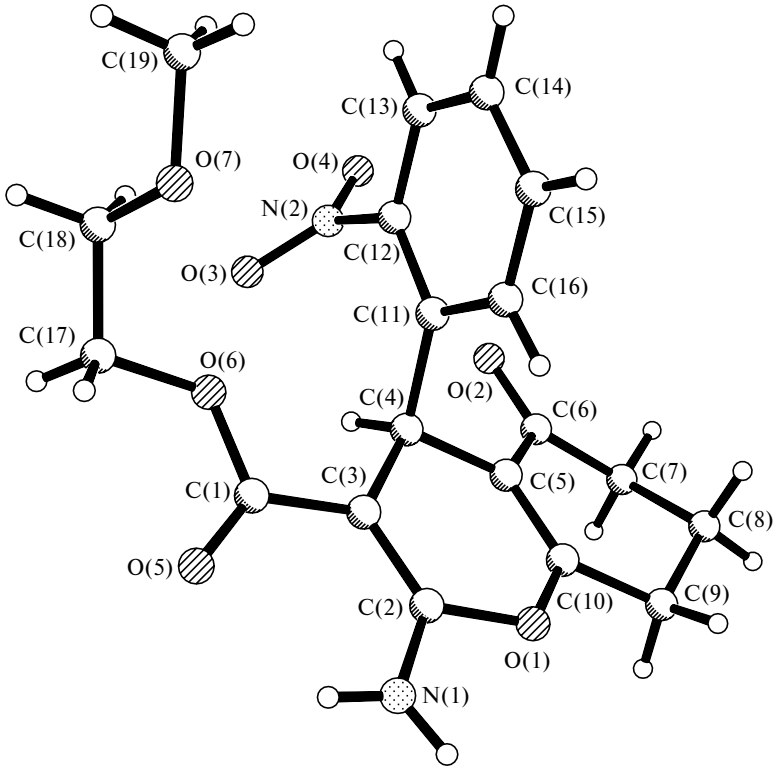


Fig 1. Overall view of the 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran molecule (**1f**).

Table 2. Bond lengths (*d*) in the 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran molecule (**1f**)

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(2)	1.370(2)	C(4)—C(5)	1.514(2)
O(1)—C(10)	1.375(2)	C(4)—C(11)	1.535(2)
O(2)—C(6)	1.215(2)	C(5)—C(10)	1.332(3)
O(3)—N(2)	1.211(2)	C(5)—C(6)	1.475(3)
O(4)—N(2)	1.225(2)	C(6)—C(7)	1.509(3)
O(5)—C(1)	1.225(2)	C(7)—C(8)	1.496(4)
O(6)—C(1)	1.344(2)	C(8)—C(9)	1.497(4)
O(6)—C(17)	1.439(2)	C(9)—C(10)	1.492(3)
O(7)—C(18)	1.408(3)	C(11)—C(16)	1.388(2)
O(7)—C(19)	1.427(3)	C(11)—C(12)	1.392(2)
N(1)—C(2)	1.333(2)	C(12)—C(13)	1.388(2)
N(2)—C(12)	1.469(2)	C(13)—C(14)	1.371(3)
C(1)—C(3)	1.445(2)	C(14)—C(15)	1.381(3)
C(2)—C(3)	1.362(2)	C(15)—C(16)	1.384(3)
C(3)—C(4)	1.520(2)	C(17)—C(18)	1.486(4)

C(2)...C(10), and C(3)...C(5) lines are characterized by rather small angles (13.0, 9.8, and 10.4°, respectively).

The cyclohexenone ring adopts a distorted half-chair conformation with the C(7) and C(8) atoms deviating from the plane of the remaining atoms (planar to within ±0.019 Å) in opposite directions by −0.156 and 0.493 Å, respectively. The dihedral angle between the bottom of the boat of the heterocycle and the plane of the fused ring is 9.4°.

The pseudoaxial *ortho*-nitrophenyl substituent is virtually perpendicular to the planar fragment of the pyran ring (dihedral angle between these fragments is 87.1°). Earlier, we have found an analogous orientation of this substituent in substituted 4-(*o*-nitrophenyl)-1,4-dihydropyridine.[17] This orientation results, apparently, from the forced intramolecular nonbonded contacts C(3)...C(16) (3.035(3) Å) and C(5)...C(16) (3.124(3) Å) whose lengths are smaller than twice the van der Waals radius of the C atom.[23] The rotation of the nitro group with respect to the benzene ring (dihedral angle is 54.0°) is noticeably larger than that observed in substituted 4-(*o*-nitrophenyl)-1,4-dihydropyridines (the corresponding dihedral angles are in the range of 31.6—44.1°).[17,18] The *ortho*-nitrophenyl substituent in the molecule under consideration, like those in substituted 1,4-dihydropyridines,[17,18] is in the synperiplanar orientation with respect to the H(4a) atom resulting in the shortened nonbonded O(3)...C(4) contact (3.079(3) Å). According to the published data,[24,25] this contact can be considered as an C—H...O hydrogen bond (C(4)—H(4a), 0.98 Å; H(4a)...O(3), 2.37 Å; C(4)—H(4a)...O(3), 128°).

As can be seen from Fig. 1, the carbonyl group is in the *cis* orientation with respect to the C(2)=C(3) bond, which leads to the formation of the strong intramolecular N(1)—H(1a)...O(5) hydrogen bond between this group and the amino group (N(1)...O(5), 2.691(2) Å; N(1)—H(1a), 0.86 Å; H(1a)...O(5), 2.09 Å; N(1)—H(1a)...O(5), 127°) and causes flattening of this fragment. This molecular structure is responsible for the redistribution of the bond lengths compared to the standard values[26] and facilitates conjugation of the amino and carbonyl groups with the C(2)=C(3) double bond.

In the crystals, molecules **1f** are linked in dimers by the intermolecular N(1)—H(1b)...O(7) hydrogen bonds ($1-x$, $2-y$, $-z$) (N(1)...O(7), 2.958(3) Å; N(1)—H(1b), 0.86 Å; H(1b)...O(7), 2.13 Å; N(1)—H(1b)...O(7), 160°).

Experimental

The melting points were measured on a Kofler stage. The IR spectra were recorded on a Perkin—Elmer 577 instrument in KBr pellets (1 : 200). The ^{1}H NMR spectra were measured on a

Table 3. Bond angles (ω) in the 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran molecule (**1f**)

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2)—O(1)—C(10)	118.52(14)	C(1)—C(3)—C(4)	120.61(15)	C(5)—C(10)—C(9)	126.34(18)
C(1)—O(6)—C(17)	117.74(16)	C(5)—C(4)—C(3)	109.46(14)	O(1)—C(10)—C(9)	110.67(16)
C(18)—O(7)—C(19)	113.1(2)	C(5)—C(4)—C(11)	109.65(13)	C(16)—C(11)—C(12)	115.61(15)
O(3)—N(2)—O(4)	123.53(16)	C(3)—C(4)—C(11)	112.61(13)	C(16)—C(11)—C(4)	119.57(15)
O(3)—N(2)—C(12)	118.88(15)	C(10)—C(5)—C(6)	118.92(16)	C(12)—C(11)—C(4)	124.78(15)
O(4)—N(2)—C(12)	117.56(16)	C(10)—C(5)—C(4)	122.50(16)	C(13)—C(12)—C(11)	123.15(17)
O(5)—C(1)—O(6)	121.55(17)	C(6)—C(5)—C(4)	118.52(16)	C(13)—C(12)—N(2)	114.47(16)
O(5)—C(1)—C(3)	126.87(18)	O(2)—C(6)—C(5)	120.69(17)	C(11)—C(12)—N(2)	122.37(15)
O(6)—C(1)—C(3)	111.57(15)	O(2)—C(6)—C(7)	122.34(19)	C(14)—C(13)—C(12)	119.24(18)
N(1)—C(2)—C(3)	127.95(18)	C(5)—C(6)—C(7)	116.91(19)	C(13)—C(14)—C(15)	119.46(17)
N(1)—C(2)—O(1)	109.60(16)	C(8)—C(7)—C(6)	112.7(2)	C(14)—C(15)—C(16)	120.25(18)
C(3)—C(2)—O(1)	122.45(16)	C(7)—C(8)—C(9)	112.4(2)	C(15)—C(16)—C(11)	122.16(17)
C(2)—C(3)—C(1)	117.68(16)	C(10)—C(9)—C(8)	110.90(19)	O(6)—C(17)—C(18)	108.62(19)
C(2)—C(3)—C(4)	121.69(16)	C(5)—C(10)—O(1)	122.97(16)	O(7)—C(18)—C(17)	109.3(2)

Bruker AC-300 spectrometer (300 MHz) in DMSO-d_6 with respect to Me_4Si.

2-Amino-4-aryl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyrans (1a—z) (general procedure). Triethylamine (0.5 mL) was added to a solution of aromatic aldehyde **4** (10 mmol), malononitrile (or cyanoacetic ester) **5** (10 mmol), and 1,3-diketone **3** (10 mmol) in EtOH (25 mL) and the reaction mixture was refluxed for 10 min. The precipitate that formed was filtered off, washed with EtOH and hexane, and recrystallized from EtOH.

2-Amino-4-(2-butoxy-3-methoxyphenyl)-3-cyano-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1a). The yield was 85%, m.p. 196—197 °C. Found (%): C, 68.51; H, 6.55; N, 7.51. $C_{21}H_{24}N_2O_4$. Calculated (%): C, 68.46; H, 6.57; N, 7.60. IR, ν/cm^{-1}: 3356, 3184 (N—H); 2194 (CN); 1680 (C=O); 1654 (δ(NH_2)). ^{1}H NMR, δ: 0.99 (t, 3 H, $O(CH_2)_3C\underline{H}_3$, J = 8.9 Hz); 1.48 (q, 2 H, $O(CH_2)_2C\underline{H}_2CH_3$, J = 8.9 Hz); 1.73 (m, 2 H, $OCH_2C\underline{H}_2Et$); 1.98 (m, 2 H, C(7)H_2); 2.29 (t, 2 H, C(6)H_2, J = 8.9 Hz); 2.62 (m, 2 H, C(8)H_2); 3.78 (s, 3 H, OMe); 3.91 (t, 2 H, OCH_2, J = 7.2 Hz); 4.17 (s, 1 H, C(4)H); 6.62 and 6.79 (both d, 1 H each, C_6H_3, J = 10.0 Hz); 6.71 (s, 3 H, NH_2, C_6H_3).

2-Amino-3-cyano-4-(5-methylfuryl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1b). The yield was 83%, m.p. 204—205 °C. Found (%): C, 66.69; H, 5.11; N, 10.35. $C_{15}H_{14}N_2O_3$. Calculated (%): C, 66.66; H, 5.22; N, 10.36. IR, ν/cm^{-1}: 3375, 3320, 3210 (N—H); 2204 (CN); 1675 (C=O); 1655 (δ(NH_2)). ^{1}H NMR, δ: 1.95 (m, 2 H, C(7)H_2); 2.18 (s, 3 H, Me); 2.32 (t, 2 H, C(6)H_2, J = 6.7 Hz); 2.59 (t, 2 H, C(8)H_2, J = 7.0 Hz); 4.26 (s, 1 H, C(4)H); 5.89 (m, 2 H, C(3′)H, C(4′)H); 6.92 (br.s, 2 H, NH_2).

2-Amino-4-(4-chlorophenyl)-3-methoxycarbonyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1c). The yield was 69%, m.p. 196—197 °C. Found (%): C, 61.45; H, 4.93; N, 4.30. $C_{17}H_{16}ClNO_4$. Calculated (%): C, 61.36; H, 4.85; N, 4.21. IR, ν/cm^{-1}: 3455, 3330 (N—H); 1690 (C=O); 1655 (δ(NH_2)). ^{1}H NMR, δ: 1.91 (m, 2 H, C(7)H_2); 2.28 (m, 2 H, C(6)H_2); 2.61 (t, 2 H, C(8)H_2, J = 6.6 Hz); 3.52 (s, 3 H, OMe); 4.57 (s, 1 H, C(4)H); 7.17 and 7.25 (both d, 2 H each, C_6H_4, J = 7.7 Hz); 7.47 (br.s, 2 H, NH_2).

2-Amino-3-methoxycarbonyl-5-oxo-4-(2-thienyl)-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1d). The yield was 69%, m.p. 196—197 °C. Found (%): C, 59.05; H, 4.87; N, 4.62. $C_{15}H_{15}NO_4S$. Calculated (%): C, 59.00; H, 4.95; N, 4.59. IR, ν/cm^{-1}: 3410, 3305 (N—H); 1690, 1660 (C=O); 1650 (δ(NH_2)). ^{1}H NMR, δ: 1.97 (m, 2 H, C(7)H_2); 2.36 (m, 2 H, C(6)H_2); 2.61 (t, 2 H, C(8)H_2, J = 6.7 Hz); 3.51 (s, 3 H, OMe); 4.90 (s, 1 H, C(4)H); 6.73 (d, 1 H, C(3′)H, J = 2.8 Hz); 6.84 (m, 1 H, C(4′)H); 7.17 (d, 1 H, C(5′)H, J = 6.0 Hz); 7.46 (br.s, 2 H, NH_2).

2-Amino-4-(2,4-difluorophenyl)-3-ethoxycarbonyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1e). The yield was 80%, m.p. 186—187 °C. Found (%): C, 61.79; H, 4.80; N, 4.00. $C_{18}H_{17}F_2NO_4$. Calculated (%): C, 61.89; H, 4.90; N, 4.01. IR, ν/cm^{-1}: 3412, 3296 (N—H); 1694 (C=O); 1654 (δ(NH_2)). ^{1}H NMR, δ: 1.12 (t, 3 H, $CH_2C\underline{H}_3$, J = 8.9 Hz); 1.97 (m, 2 H, C(7)H_2); 2.26 (m, 2 H, C(6)H_2); 2.62 (t, 2 H, C(8)H_2, J = 7.0 Hz); 3.97 (q, 2 H, OCH_2, J = 8.9 Hz); 4.69 (s, 1 H, C(4)H); 6.78 (m, 2 H, C_6H_3); 7.19 (m, 1 H, C_6H_3); 7.39 (br.s, 2 H, NH_2).

2-Amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1f). The yield was 78%, m.p. 135 °C. Found (%): C, 58.80; H, 5.29; N, 7.17. $C_{19}H_{20}N_2O_7$. Calculated (%): C, 58.76; H, 5.19; N, 7.21. IR, ν/cm^{-1}: 3404, 3280 (N—H); 1692, 1688 (C=O); 1670 (δ(NH_2)). ^{1}H NMR, δ: 1.86 (m, 2 H, C(7)H_2); 2.22 (m, 2 H, C(6)H_2); 2.58 (t, 2 H, C(8)H_2, J = 6.4 Hz); 3.07 (s, 3 H, OMe); 3.29 (t, 2 H, $C\underline{H}_2OMe$, J = 4.0 Hz); 3.88 and 4.00 (both m, 1 H each, $COOCH_2$); 5.41 (s, 1 H, C(4)H); 7.30 and 7.54 (both t, 1 H each, C(4′)H, C(5′)H, J = 8.0 Hz); 7.32 and 7.74 (both d, 1 H each, C(3′)H, C(6′)H, J = 8.0 Hz); 7.64 (br.s, 2 H, NH_2).

2-Amino-3-(2-methoxyethoxycarbonyl)-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1g). The yield was 84%, m.p. 155 °C. Found (%): C, 58.78; H, 5.26; N, 7.31. $C_{19}H_{20}N_2O_7$. Calculated (%): C, 58.76; H, 5.19; N, 7.21. IR, ν/cm^{-1}: 3392, 3272 (N—H); 1696 (C=O); 1636 (δ(NH_2)). ^{1}H NMR, δ: 1.93 (m, 2 H, C(7)H_2); 2.29 (m, 2 H, C(6)H_2); 2.66 (m, 2 H, C(8)H_2); 3.17 (s, 3 H, OMe); 3.41 (m, 2 H, $C\underline{H}_2OMe$); 4.04 (m, 2 H, $COOCH_2$); 4.68 (s, 1 H, C(4)H); 7.52 (t, 1 H, C(5′)H, J = 9.0 Hz); 7.61 (m, 3 H, C_6H_4, NH_2); 7.97 (m, 2 H, C_6H_4).

2-Amino-3-(2-methoxyethoxycarbonyl)-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1h). The yield was 72%, m.p. 171 °C. Found (%): C, 58.74; H, 5.30; N, 7.18. $C_{19}H_{20}N_2O_7$. Calculated (%): C, 58.76; H, 5.19; N, 7.21. IR, ν/cm^{-1}: 3456, 3328 (N—H); 1688 (C=O); 1656 (δ(NH_2)). ^{1}H NMR, δ: 1.92 (m, 2 H, C(7)H_2); 2.29 (m, 2 H, C(6)H_2); 2.65 (m, 2 H, C(8)H_2); 3.23 (s, 3 H, OMe); 3.45 (m, 2 H, $C\underline{H}_2OMe$); 4.05 (t, 2 H, $COOCH_2$, J = 5.9 Hz); 4.67 (s, 1 H, C(4)H); 7.44 and 8.08 (both d, 2 H each, C_6H_4, J = 9.9 Hz); 7.61 (br.s, 2 H, NH_2).

2-Amino-3-(2-methoxyethoxycarbonyl)-5-oxo-4-(3-pyridyl)-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1i). The yield was 61%, m.p. 153—154 °C. Found (%): C, 62.66; H, 5.84; N, 8.09. $C_{18}H_{20}N_2O_5$. Calculated (%): C, 62.78; H, 5.85; N, 8.13. IR, ν/cm^{-1}: 3400, 3264 (N—H); 1688 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 1.97 (m, 2 H, C(7)H_2); 2.29 (m, 2 H, C(6)H_2); 2.63 (m, 2 H, C(8)H_2); 3.23 (s, 3 H, OMe); 3.42 (m, 2 H, $C\underline{H}_2OMe$); 4.04 (m, 2 H, $COOCH_2$); 4.52 (s, 1 H, C(4)H); 7.14 and 8.32 (both d, 2 H each, C_5H_4N, J = 6.7 Hz); 7.57 (s, 2 H, NH_2).

2-Amino-3-cyano-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1j). The yield was 77%, m.p. 257 °C (decomp.). Found (%): C, 63.73; H, 5.00; N, 12.36. $C_{18}H_{17}N_3O_4$. Calculated (%): C, 63.71; H, 5.05; N, 12.38. IR, ν/cm^{-1}: 3472, 3336, 3256 (N—H); 2192 (CN); 1688 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 0.90 and 1.03 (both s, 3 H each, C(7)Me_2); 2.11 (m, 2 H, C(6)H_2); 2.50* (m, 2 H, C(8)H_2); 4.96 (s, 1 H, C(4)H); 7.06 (br.s, 2 H, NH_2); 7.35 and 7.82 (both d, 1 H each, C(3′)H, C(6′)H, J = 7.6 Hz); 7.42 and 7.65 (both t, 1 H each, C(4′)H, C(5′)H, J = 7.6 Hz).

2-Amino-3-cyano-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1k). The yield was 89%, m.p. 223—224 °C. Found (%): C, 63.78; H, 5.03; N, 12.47. $C_{18}H_{17}N_3O_4$. Calculated (%): C, 63.71; H, 5.05; N, 12.38. IR, ν/cm^{-1}: 3432, 3336, 3200 (N—H); 2184 (CN); 1680 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 0.96 and 1.07 (both s, 3 H each, C(7)Me_2); 2.21 (m, 2 H, C(6)H_2); 2.55 (s, 2 H, C(8)H_2); 4.43 (s, 1 H, C(4)H); 7.13 (s, 2 H, NH_2); 7.66 (m, 2 H, C_6H_4); 7.97 (s, 1 H, C(2′)H); 8.09 (d, 1 H, C_6H_4, J = 9.0 Hz).

* The signals for the protons of the C(8)H_2 methylene group in the spectra of compounds **1j,m—q,s,u,w** overlap with the signal for the protons of DMSO-d_6.

2-Amino-3-cyano-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1l). The yield was 82%, m.p. 143 °C. Found (%): C, 63.73; H, 5.11; N, 12.44. $C_{18}H_{17}N_3O_4$. Calculated (%): C, 63.71; H, 5.05; N, 12.38. IR, ν/cm^{-1}: 3392, 3328, 3216 (N—H); 2192 (CN); 1684 (C=O); 1656 (δ(NH_2)). ^{1}H NMR, δ: 0.96 and 1.05 (both s, 3 H each, C(7)Me_2); 2.19 (m, 2 H, C(6)H_2); 2.54 (m, 2 H, C(8)H_2); 4.38 (s, 1 H, C(4)H); 7.12 (s, 2 H, NH_2); 7.45 and 8.17 (both d, 2 H each, C_6H_4, J = 8.8 Hz).

2-Amino-3-cyano-4-(2,4,5-trimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1m). The yield was 83%, m.p. 111—112 °C. Found (%): C, 65.64; H, 6.23; N, 7.27. $C_{21}H_{24}N_2O_5$. Calculated (%): C, 65.61; H, 6.29; N, 7.29. IR, ν/cm^{-1}: 3344, 3192 (N—H); 2196 (CN); 1688 (C=O); 1662 (δ(NH_2)). ^{1}H NMR, δ: 1.03 and 1.12 (both s, 3 H each, C(7)Me_2); 2.14 (m, 2 H, C(6)H_2); 2.50 (s, 2 H, C(8)H_2); 3.19 (s, 3 H, C(2′)OMe); 3.29 (s, 6 H, C(4′)OMe, C(5′)OMe); 4.39 (s, 1 H, C(4)H); 6.47 (br.s, 2 H, NH_2); 6.53 and 6.57 (both s, 1 H each, C_6H_2).

2-Amino-3-cyano-4-(3-methoxy-4-propoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1n). The yield was 77%, m.p. 157—158 °C. Found (%): C, 69.07; H, 6.87; N, 7.33. $C_{22}H_{26}N_2O_4$. Calculated (%): C, 69.09; H, 6.85; N, 7.32. IR, ν/cm^{-1}: 3340, 3190 (N—H); 2200 (CN); 1680 (C=O); 1650 (δ(NH_2)). ^{1}H NMR, δ: 1.02 (t, 3 H, O(CH_2)$_2$C$\underline{H}_3$, J = 8.3 Hz); 1.02 and 1.09 (both s, 3 H each, C(7)Me_2); 1.76 (q, 2 H, C$\underline{H}_2$$CH_3$, J = 8.3 Hz); 2.16 (m, 2 H, C(6)H_2); 2.49 (s, 2 H, C(8)H_2); 3.77 (s, 3 H, OMe); 3.87 (t, 2 H, OCH_2, J = 8.9 Hz); 4.12 (s, 1 H, C(4)H); 6.63 and 6.78 (both d, 1 H each, C(5′)H, C(6′)H, J = 10.0 Hz); 6.68 (s, 3 H, NH_2, C(2′)H).

2-Amino-4-(2-chloro-3,4-methylenedioxyphenyl)-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1o). The yield was 93%, m.p. 255 °C (decomp.). Found (%): C, 61.10; H, 4.71; N, 7.53. $C_{19}H_{17}ClN_2O_4$. Calculated (%): C, 61.22; H, 4.59; N, 7.51. IR, ν/cm^{-1}: 3332, 3256, 3212 (N—H); 2188 (CN); 1688 (C=O); 1670 (δ(NH_2)). ^{1}H NMR, δ: 1.02 and 1.06 (both s, 3 H each, C(7)Me_2); 2.17 (m, 2 H, C(6)H_2); 2.51 (s, 2 H, C(8)H_2); 4.62 (s, 1 H, C(4)H); 6.01 (d, 2 H, OCH_2O, J = 1.1 Hz); 6.64 (s, 1 H, C(5′)H); 6.80 (br.s, 2 H, NH_2); 6.91 (s, 1 H, C(6′)H).

2-Amino-4-(4-carbamoylmethoxy)phenyl-3-cyano-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1p). The yield was 89%, m.p. 201—202 °C. Found (%): C, 65.35; H, 5.63; N, 11.50. $C_{20}H_{21}N_3O_4$. Calculated (%): C, 65.38; H, 5.76; N, 11.44. IR, ν/cm^{-1}: 3380, 3324, 3192 (N—H); 2194 (CN); 1682 (C=O); 1650 (δ(NH_2)). ^{1}H NMR, δ: 1.01 and 1.10 (both s, 3 H each, C(7)Me_2); 2.15 (m, 2 H, C(6)H_2); 2.49 (s, 2 H, C(8)H_2); 4.16 (s, 1 H, C(4)H); 4.33 (s, 2 H, OCH_2); 6.68 (br.s, 2 H, C(2)NH_2); 6.84 and 7.09 (both d, 2 H each, C_6H_4, J = 10.2 Hz); 7.22 (br.s, 2 H, C(O)NH_2).

2-Amino-3-cyano-7,7-dimethyl-4-(4-morpholinophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1q). The yield was 79%, m.p. 226 °C (decomp.). Found (%): C, 69.70; H, 6.63; N, 10.96. $C_{22}H_{25}N_3O_4$. Calculated (%): C, 69.63; H, 6.64; N, 11.07. IR, ν/cm^{-1}: 3450, 3308, 3200 (N—H); 2200 (CN); 1686 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 1.01 and 1.11 (both s, 3 H each, C(7)Me_2); 2.15 (m, 2 H, C(6)H_2); 2.49 (s, 2 H, C(8)H_2); 3.09 (m, 4 H, CH_2—N—CH_2); 3.74 (m, 4 H, CH_2—O—CH_2); 4.11 (s, 1 H, C(4)H); 6.60 (s, 2 H, NH_2); 6.79 and 7.03 (both d, 2 H each, C_6H_4).

2-Amino-3-cyano-4-[3-methoxy-4-(2-morpholinoethoxy)phenyl]-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1r). The yield was 67%, m.p. 169—170 °C. Found (%): C, 66.11; H, 6.81; N, 9.34. $C_{25}H_{31}N_3O_5$. Calculated (%): C, 66.21; H, 6.89; N, 9.26. IR, ν/cm^{-1}: 3332 (N—H); 2192 (CN); 1688 (C=O); 1674 (δ(NH_2)). ^{1}H NMR, δ: 1.01 and 1.09 (both s, 3 H each, C(7)Me_2); 2.16 (m, 2 H, C(6)H_2); 2.49 (s, 2 H, C(8)H_2); 2.69 (t, 2 H, C_6H_3—$OCH_2C\underline{H}_2N$, J = 5.0 Hz); 3.10* (m, 4 H, CH_2—N—CH_2); 3.58 (m, 4 H, CH_2—O—CH_2); 3.77 (s, 3 H, OMe); 4.02 (t, 2 H, PhO$C\underline{H}_2CH_2N$, J = 5.0 Hz); 4.12 (s, 1 H, C(4)H); 6.62 and 6.81 (both d, 1 H each, C(5′)H, C(6′)H, J = 10.5 Hz); 6.68 (s, 3 H, NH_2, C(2′)H).

2-Amino-4-(2-fluorophenyl)-3-methoxycarbonyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1s). The yield was 59%, m.p. 201—202 °C. Found (%): C, 65.95; H, 5.94; N, 4.18. $C_{19}H_{20}FNO_4$. Calculated (%): C, 66.08; H, 5.84; N, 4.06. IR, ν/cm^{-1}: 3428, 3312 (N—H); 1696, 1670 (C=O); 1656 (δ(NH_2)). ^{1}H NMR, δ: 0.89 and 1.04 (both s, 3 H each, C(7)Me_2); 2.16 (m, 2 H, C(6)H_2); 2.49 (m, 2 H, C(8)H_2); 3.48 (s, 3 H, OMe); 4.68 (s, 1 H, C(4)H); 7.08 (m, 4 H, C_6H_4); 7.49 (br.s, 2 H, NH_2).

2-Amino-4-(2,4-difluorophenyl)-3-ethoxycarbonyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1t). The yield was 72%, m.p. 204—205 °C. Found (%): C, 63.56; H, 5.57; N, 3.78. $C_{20}H_{21}F_2NO_4$. Calculated (%): C, 63.65; H, 5.61; N, 3.71. IR, ν/cm^{-1}: 3424, 3312 (N—H); 1694, 1670 (C=O); 1656 (δ(NH_2)). ^{1}H NMR, δ: 0.96 and 1.09 (both s, 3 H each, C(7)Me_2); 1.11 (t, 3 H, $CH_2C\underline{H}_3$, J = 8.0 Hz); 2.13 (m, 2 H, C(6)H_2); 2.47 (m, 2 H, C(8)H_2); 3.94 (q, 2 H, $OC\underline{H}_2CH_3$, J = 8.0 Hz); 4.67 (s, 1 H, C(4)H); 6.77 (m, 2 H, C_6H_3); 7.17 (m, 1 H, C_6H_3); 7.39 (br.s, 2 H, NH_2).

2-Amino-3-isopropyloxycarbonyl-4-(4-methoxycarbonylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1u). The yield was 81%, m.p. 195—196 °C. Found (%): C, 66.70; H, 6.61; N, 3.42. $C_{23}H_{27}NO_6$. Calculated (%): C, 66.81; H, 6.58; N, 3.39. IR, ν/cm^{-1}: 3412, 3300 (N—H); 1688 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 0.91 and 1.21 (both d, 3 H each, OCH($C\underline{H}_3$)$_2$, J = 6.6 Hz); 0.92 and 1.09 (both s, 3 H each, C(7)Me_2); 2.13 (m, 2 H, C(6)H_2); 2.48 (m, 2 H, C(8)H_2); 3.82 (s, 3 H, OMe); 4.53 (s, 1 H, C(4)H); 4.79 (m, 1 H, O$C\underline{H}Me_2$); 7.26 and 7.78 (both d, 2 H each, C_6H_4, J = 9.4 Hz); 7.43 (br.s, 2 H, NH_2).

2-Amino-3-*tert*-butoxycarbonyl-4-(4-methoxycarbonylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1v). The yield was 59%, m.p. 207—208 °C. Found (%): C, 67.44; H, 6.90; N, 3.21. $C_{24}H_{29}NO_6$. Calculated (%): C, 67.43; H, 6.84; N, 3.28. IR, ν/cm^{-1}: 3436, 3320 (N—H); 1690, 1682 (C=O); 1668 (δ(NH_2)). ^{1}H NMR, δ: 0.91 and 1.08 (both s, 3 H each, C(7)Me_2); 1.28 (s, 9 H, $OCMe_3$); 2.12 (m, 2 H, C(6)H_2); 2.48 (m, 2 H, C(8)H_2); 3.82 (s, 3 H, OMe); 4.49 (s, 1 H, C(4)H); 7.26 and 7.79 (both d, 2 H each, C_6H_4, J = 9.4 Hz); 7.37 (br.s, 2 H, NH_2).

2-Amino-3-(2-methoxyethoxycarbonyl)-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1w). The yield was 93%, m.p. 116 °C. Found (%): C, 60.62; H, 5.72;

* The signals for the protons of the methylene groups in the spectra of compounds **1r,x** overlap with the signal for the protons of water present in DMSO-d_6, which was used in NMR spectroscopic studies.

N, 6.84. $C_{21}H_{24}N_2O_7$. Calculated (%): C, 60.57; H, 5.81; N, 6.73. IR, ν/cm^{-1}: 3392, 3288 (N—H); 1692 (C=O); 1664 (δ(NH_2)). ^{1}H NMR, δ: 0.93 and 1.06 (both s, 3 H each, C(7)Me_2); 2.19 (m, 2 H, C(6)H_2); 2.56 (m, 2 H, C(8)H_2); 3.18 (s, 3 H, OMe); 3.42 (m, 2 H, C$\underline{H}_2$OMe); 4.03 (m, 2 H, COOCH_2); 4.65 (s, 1 H, C(4)H); 7.52 (t, 1 H, C(5′)H, J = 10.3 Hz); 7.61 (br.s, 3 H, NH_2, C(2′)H); 7.98 (m, 2 H, C(4′)H, C(6′)H).

2-Amino-3-(2-methoxyethoxycarbonyl)-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1x). The yield was 80%, m.p. 183 °C. Found (%): C, 60.51; H, 5.68; N, 6.85. $C_{21}H_{24}N_2O_7$. Calculated (%): C, 60.57; H, 5.81; N, 6.73. IR, ν/cm^{-1}: 3376, 3256 (N—H); 1696 (C=O); 1656 (δ(NH_2)). ^{1}H NMR, δ: 0.92 and 1.07 (both s, 3 H each, C(7)Me_2); 2.19 (m, 2 H, C(6)H_2); 2.55 (m, 2 H, C(8)H_2); 3.20 (s, 3 H, OMe); 3.44 (m, 2 H, C$\underline{H}_2$OMe); 4.04 (t, 2 H, COOCH_2, J = 4.0 Hz); 4.64 (s, 1 H, C(4)H); 7.43 and 8.08 (both d, 2 H each, C_6H_4, J = 9.5 Hz); 7.60 (br.s, 2 H, NH_2).

2-Amino-3-(2-methoxyethoxycarbonyl)-7,7-dimethyl-5-oxo-4-(4-pyridyl)-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1y). The yield was 61%, m.p. 156—157 °C. Found (%): C, 64.51; H, 6.61; N, 7.55. $C_{20}H_{24}N_2O_5$. Calculated (%): C, 64.50; H, 6.50; N, 7.52. IR, ν/cm^{-1}: 3384, 3256 (N—H); 1690, 1675 (C=O); 1660 (δ(NH_2)). ^{1}H NMR, δ: 0.94 and 1.09 (both s, 3 H each, C(7)Me_2); 2.15 (m, 2 H, C(6)H_2); 2.50 (m, 2 H, C(8)H_2); 3.25 (s, 3 H, OMe); 3.42 (m, 2 H, OCH_2); 4.03 (m, 2 H, OCH_2); 4.49 (s, 1 H, C(4)H); 7.12 and 8.33 (both d, 2 H each, C_5H_4N, J = 5.0 Hz); 7.57 (br.s, 2 H, NH_2).

2-Amino-3-benzyloxycarbonyl-4-(4-methoxycarbonylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (1z). The yield was 87%, m.p. 193 °C. Found (%): C, 70.15; H, 5.97; N, 2.96. $C_{27}H_{27}NO_6$. Calculated (%): C, 70.27; H, 5.90; N, 3.04. IR, ν/cm^{-1}: 3400, 3292 (N—H); 1692, 1670 (C=O); 1652 (δ(NH_2)). ^{1}H NMR, δ: 0.90 and 1.09 (both s, 3 H each, C(7)Me_2); 2.12 (m, 2 H, C(6)H_2); 2.49 (m, 2 H, C(8)H_2); 3.83 (s, 3 H, OMe); 4.60 (s, 1 H, C(4)H); 4.97 (m, 2 H, OCH_2); 7.04 (m, 2 H, C_6H_5); 7.22 (m, 5 H, C_6H_5 (3 H), C_6H_4 (2 H)); 7.56 (br.s, 2 H, NH_2); 7.74 (d, 2 H, C_6H_4, J = 10.4 Hz).

2-Amino-1,3,3-tricyano-4-phenyl-3,4,4a,5,6,7-hexahydronaphthalene (9). A mixture of equimolar amounts (10 mmol) of cyclohexanone (**7**) and phenylmethylenemalononitrile was refluxed in EtOH (10 mL) in the presence of a catalytic amount of Et_3N (2 drops) for 10 min. The precipitate that formed was filtered off and recrystallized from EtOH. The yield was 24%, m.p. 259—261 °C (*cf.* lit. data[27]: m.p. 260—265 °C). Found (%): C, 75.93; H, 5.35; N, 18.55. $C_{19}H_{16}N_4$. Calculated (%): C, 75.98; H, 5.37; N, 18.65. IR, ν/cm^{-1}: 3424, 3340, 3256, 3232 (N—H); 2212 (CN); 1650 (δ(NH_2)). ^{1}H NMR, δ: 0.92 (m, 1 H, C(4a)H); 1.50 (m, 2 H, C(5)H_2); 1.73 and 2.11 (both m, 1 H each, C(6)H_2); 2.21 and 2.78 (both m, 1 H each, C(7)H_2); 3.31 (d, 1 H, C(4)H, J = 11.7 Hz); 5.78 (s, 1 H, C(8)H); 7.07 (s, 2 H, NH_2); 7.46 (m, 5 H, C_6H_5).

X-ray diffraction analysis of compound 1f. Colorless crystals of 2-amino-3-(2-methoxyethoxycarbonyl)-4-(2-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran (**1f**) ($C_{19}H_{20}N_2O_7$) belong to the monoclinic system, at 25 °C: a = 8.455(2), b = 8.916(2), c = 24.670(5) Å, β = 96.93(2)°, V = 1846.1(6) Å^3, d_{calc} = 1.397 g cm^{-3}, Z = 4, space group $P2_1/n$.

The unit cell parameters and intensities of 4278 reflections were measured on an automated four-circle Siemens diffractometer (λ-Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 27°).

The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonohydrogen atoms. The positions of the H atoms were calculated geometrically and refined using the riding model. The final reliability factors were as follows: R_1 = 0.054 based on 3090 independent reflections and wR_2 = 0.1479 based on 4007 reflections. All calculations were carried out with the use of the SHELXL97 program package.[28] The atomic coordinates and isotropic equivalent thermal parameters of the nonhydrogen atoms were deposited with the Cambridge Structural Database.

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