Chemistry of Heterocyclic Compounds, Vol. 40, No. 7, 2004

11-ARYL-3,3-DIMETHYL-7- AND 7,8-SUBSTITUTED 1,2,3,4,10,11-HEXAHYDRO-5H-DIBENZO[*b,e*]-1,4-DIAZEPIN-1-ONES

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In reactions of 3-(5- and 5,6-substituted 2-aminophenylamino)-5,5-dimethylcyclohex-2-en-ones with carbaldehydes of pyridine, thiophene, and furan and substituted benzaldehydes, we have obtained 21 novel 7H-7-methoxycarbonyl-, 7-benzoyl-, 7-trifluoromethyl-, 7-nitro- and 7,8-dichloro-11-aryl-3,3-dimethyl-1,2,3,4,10,11-hexahydro-5H-dibenzo[b,e]-1,4-diazepin-1-one.

Keywords: dimedone, substituted 1,2-phenylenediamines, pyridine-, thiophene-, furancarbaldehydes, dibenzo[*b,e*]-1,4-diazepine derivatives.

Modification of dibenzo[*b,e*]-1,4-diazepines is part of extensive research on synthesis of derivatives of tricyclic systems including a 1,4-diazepine moiety, among which pyrido[2,3-*b*]benzo[*e*]-1,4-diazepines and dipyrido[3,2-*b*:2,3-*e*]-1,4-diazepines are key derivatives according to the criterion of pharmacological value [1-11].

In an extension of [12], in this study we obtained dibenzo[*e*]-1,4-diazepines by the method used in [13-16]: reaction of 3-(2-aminophenylamino)-5,5-dimethylcyclohex-2-en-1-ones with pyridine-, thiophene-, furancarbaldehydes and substituted benzaldehydes.

By boiling 1,2-phenylenediamines **1a-f** with dimedone **2** in toluene in the presence of catalytic amounts of *p*-toluenesulfonic acid under conditions for azeotropic distillation of water, we obtained (2-aminophenyl)aminocyclohexenes **3a-f**. When using 5-substituted 1,2-phenylenediamines **1b-e**, two isomeric enaminones could be formed. In the ^{1}H NMR spectra of the latter, we observe a broadened two-proton signal from the primary amino group in the 3.76-5.81 ppm region, one six-proton singlet from the methyl groups and two two-proton singlets from the CH_2 groups of the dimedone moiety. The proton at the $C_{(2)}$ atom absorbs in the interval 4.65-5.07 ppm, while the enamine NH proton absorbs downfield at 7.56-8.23 ppm. The spatial proximity of the enamine NH and aromatic $C_{(6)}$–H protons is proven based on ^{1}H NMR difference spectroscopy (NOE), which made it possible to choose in favor of the structures **3b-e**.

The reaction of enamines **3a-f** with substituted benzaldehydes, 2-, 3-, 4-pyridinecarbaldehydes, 2-thiophenecarbaldehyde (**4a-j**) was carried out by boiling in ethanol in the presence of catalytic amounts of H_2SO_4, while the reaction with furfural **4k** was carried out in the presence of piperidine acetate.

The structure of the dibenzodiazepines in **5a-u** was confirmed by IR and ^{1}H NMR spectra. In the ^{1}H NMR spectra, the methyl groups of the dimedone moiety are magnetically nonequivalent, and are detected as two three-proton singlets in the 0.98-1.05 ppm range. The protons from one of the methylene groups are also magnetically nonequivalent in some diazepines **5**, and their absorption is represented by an AB spin system with geminal constant 16-18 Hz.

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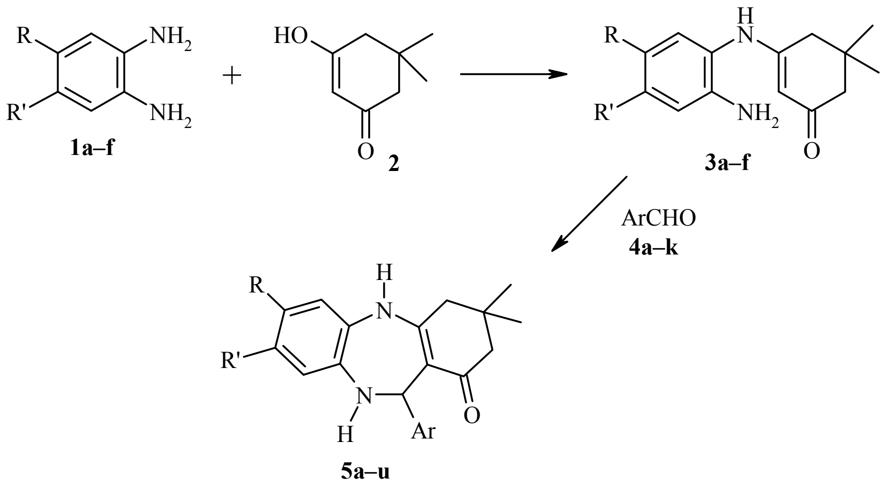

1, **3** **a** R = R' = H; **b** R = COOMe, R' = H; **c** R = COPh, R' = H; **d** R = CF_3, R' = H**;** **e** R = NO_2, R' = H; **f** R = R' = Cl;
4 **a** Ar = $C_6H_3F_2$-3,5; **b** Ar = $C_6H_3O_2CH_2$-3,4; **c** Ar = $C_6H_4NO_2$-3; **d** Ar = C_6H_4Cl-4; **e** Ar = C_6H_4F-4;
f Ar = $C_6H_3(OMe)_2$-3,4; **g** Ar = 2-pyridyl, **h** Ar = 3-pyridyl, **i** Ar = 4-pyridyl, **j** Ar = 2-thienyl, **k** Ar = 2-furyl;
5 **a-r** R' = H, **s-u** R' = Cl; **a** R = H, Ar = $C_6H_3F_2$-3,5; **b** R = H, Ar = 2-pyridyl; **c** R = H, Ar = 3-pyridyl;
d R = H, Ar = 4-pyridyl; **e** R = COOMe, Ar = $C_6H_3O_2CH_2$-3,4; **f** R = COOMe, Ar = $C_6H_3F_2$-3,5; **g** R = COOMe, Ar = 3-pyridyl;
h R = COOMe, Ar = 4-pyridyl; **i** R = COPh, Ar = $C_6H_4NO_2$-3; **j** R = COPh, Ar = 4-pyridyl; **k** R = COPh, Ar = 2-thienyl;
l R = COPh, Ar = 2-furyl; **m** R = CF_3, Ar = C_6H_4Cl-4; **n** R = CF_3, Ar = C_6H_4F-4; **o** R = CF_3, Ar = 2-thienyl;
p R = CF_3, Ar = 2-furyl; **q** R = NO_2, Ar = 2-thienyl; **r** R = NO_2, Ar = 2-furyl; **s** R = Cl,
Ar = $C_6H_3(OMe)_2$-3,4; **t** R = Cl, Ar = $C_6H_3F_2$-3,5; **u** R = Cl, Ar = 4-pyridyl

The signals from the protons at the tertiary $C_{(11)}$ atom are detected as doublets in the interval δ 5.68-6.82 ppm with vicinal spin–spin coupling constant 5 Hz. The $N_{(10)}$–H proton is represented by such a doublet (δ 6.58-5.53) in most of the diazepines **5**, except in cases when it is overlapped by aromatic signals. The $N_{(5)}$–H signals resonate downfield: δ 8.93-9.12 ppm.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 for suspensions of the compounds in vaseline oil (1800-1500 cm^{-1} region) and in hexachlorobutadiene (3600-2000 cm^{-1} region). In the 1800-1500 cm^{-1} region, only the carbonyl frequencies are given. The frequencies of the stretching vibrations of the C–H bond in the 3050-2800 cm^{-1} region are not given. The ^1H NMR spectra were recorded on a Bruker WH/90DS (90 MHz), internal standard TMS.

In this work, we used diamines and aldehydes from Lancaster, Acros, and Fluka.

To monitor the course of the reactions, we used Merck Silica Gel 60 F254 plates, with the systems 7:3 ethyl acetate–toluene (A), 4:3 ethyl acetate–toluene (B); visualization by heating and exposure to UV light.

3-(2-Aminophenylamino)-5,5-dimethylcyclohex-2-en-1-one (3a) was obtained by the procedure in [13].

3-(2-Amino-5-methoxycarbonylphenylamino)- (3b), 3-(2-Amino-5-benzoylphenylamino)- (3c), 3-(2-Amino-5-trifluoromethylphenylamino)- (3d), 3-(2-Amino-5-nitrophenylamino)- (3e), 3-(2-Amino-4,5-dichlorophenylamino)- (3f) 5,5-dimethylcyclohex-2-en-1-ones. Dimedone **2** (5 mmol) and the corresponding diamine **1b-f** (5 mmol) were boiled in toluene (100 ml) in the presence of catalytic amounts of *p*-toluenesulfonic acid under conditions for azeotropic distillation of water for 3 h. The enamine **3e** that precipitated upon cooling

TABLE 1. Characteristics of Synthesized Compounds

Compound	Empirical formula	Found, % Calculated, %				mp, °C	Yield, %
		C	H	N	Cl (S)		
3b	$C_{16}H_{20}N_2O_3$	66.65 66.65	6.77 6.99	9.84 9.72		213-214	35
3c	$C_{21}H_{22}N_2O_2$	75.25 75.42	6.60 6.63	8.31 8.38		145-146	66
3d	$C_{15}H_{17}F_3N_2O$	60.50 60.39	5.71 5.75	9.18 9.39		211-211	81
3e	$C_{14}H_{17}N_3O_3$	60.89 61.08	6.15 6.23	15.11 15.26		204-206	55
3f	$C_{14}H_{16}Cl_2N_2O$	56.16 56.20	5.50 5.39	9.29 9.36	23.50 23.70	218-219	54
5a	$C_{21}H_{20}F_2N_2O$	71.02 71.17	5.60 5.69	7.79 7.90		247-248	46
5b	$C_{20}H_{21}N_3O$	75.01 75.20	6.48 6.63	13.13 13.16		230-233	53
5c	$C_{20}H_{21}N_3O$	75.14 75.20	6.60 6.63	13.97 13.16		216-218	94
5d	$C_{20}H_{21}N_3O$	75.05 75.20	6.66 6.63	13.11 13.16		260-263	88
5e	$C_{24}H_{24}N_2O_5$	68.73 68.56	5.70 5.75	6.52 6.66		235-236	36
5f	$C_{23}H_{22}F_2N_2O_3$	67.11 66.98	5.30 5.38	6.68 6.79		181-182	60
5g	$C_{22}H_{23}N_3O_3$	70.17 70.01	6.09 6.14	11.10 11.13		261-263	54
5h	$C_{22}H_{23}N_3O_3$	69.84 70.01	6.02 6.14	11.18 11.13		280-281	53
5i	$C_{28}H_{25}N_3O_4$	71.79 71.93	5.30 5.39	8.79 8.99		263-265	87
5j	$C_{27}H_{25}N_3O_2$	76.66 76.57	5.82 5.95	10.01 9.92		266-269	51
5k	$C_{26}H_{24}N_2O_2S$	72.67 72.87	5.60 5.65	6.43 6.54	(7.30) (7.48)	284-285	42
5l	$C_{26}H_{24}N_2O_3$	75.80 75.71	5.81 5.86	6.65 6.79		269-271	87
5m	$C_{22}H_{20}ClF_3N_2O$	62.61 62.78	4.80 4.79	6.55 6.66		220-222	86
5n	$C_{22}H_{20}F_4N_2O$	65.15 65.34	4.91 4.99	6.81 6.93		206-207	74
5o	$C_{20}H_{19}F_3N_2OS$	61.11 61.21	4.97 4.88	7.00 7.14	(8.40) (8.17)	258-260	80
5p	$C_{20}H_{19}F_3N_2O_2$	63.65 63.82	5.01 5.09	7.28 7.44		269-271	78
5q	$C_{19}H_{19}N_3O_3S$	61.60 61.77	5.13 5.18	11.21 11.37	(8.70) (8.68)	289-290	68
5r	$C_{19}H_{19}N_3O_4$	64.43 64.58	5.30 5.42	11.70 11.89		278-280	77
5s	$C_{23}H_{24}Cl_2N_2O_3$	61.54 61.75	5.32 5.41	6.12 6.26	15.60 15.85	188-189	45
5t	$C_{21}H_{18}Cl_2F_2N_2O$	59.40 59.59	4.25 4.29	6.49 6.62	16.60 16.75	149-151	83
5u	$C_{20}H_{19}Cl_2N_3O$	61.66 61.86	4.90 4.93	10.75 10.82	18.10 18.26	266-268	51

was recrystallized from toluene. In the rest of the cases, the toluene was completely driven off on a rotary evaporator, the dry residue (with addition of activated carbon) was recrystallized from THF (compounds **3c,d**), toluene (compound **3b**), or ethanol (compound **3f**).

TABLE 2. Spectral Characteristics of Synthesized Compounds

Compound	IR spectrum ν, cm^{-1}	^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (SSCC, *J*, Hz)
1	2	3
3b	1706, 1630; 3460, 3330, 3220	1.03 (6H, s, 2CH$_3$); 2.03 (2H, s, CH$_2$); 2.43 (2H, s, CH$_2$); 3.78 (3H, s, OCH$_3$); 4.65 (1H, d, =CH); 5.81 (2H, br. s, NH$_2$); 6.74 (1H, d, ^3J = 8, C$_6$H$_3$); 7.44 (1H, d, ^4J = 2, C$_6$H$_3$); 7.56 (1H, dd, ^3J = 8, ^4J = 2, C$_6$H$_3$); 8.09 (1H, br. s, NH)
3c	1645, 1625; 3480, 3280, 3200	0.95 (6H, s, 2CH$_3$); 1.96 (2H, s, CH$_2$); 2.33 (2H, s, CH$_2$); 4.62 (1H, s, =CH); 5.93 (2H, br. s, NH$_2$); 6.77 (1H, d, ^3J = 8, C$_6$H$_3$); 7.36-7.64 (7H, m, C$_6$H$_5$, C$_6$H$_3$); 8.16 (1H, br. s, NH)
3d	1630; 3450, 3300, 3180	0.97 (6H, s, 2CH$_3$); 1.96 (2H, s, CH$_2$); 2.33 (2H, s, CH$_2$); 4.56 (1H, s, =CH); 5.58 (2H, br. s, NH$_2$); 6.82 (1H, d, ^3J = 8, C$_6$H$_3$); 7.11 (1H, d, ^4J = 2, C$_6$H$_3$); 7.29 (1H, dd, ^3J = 8, ^4J = 2, C$_6$H$_3$); 8.17 (1H, br. s, NH)
3e	1635; 3480, 3340, 3240	1.01 (6H, s, 2CH$_3$); 2.02 (2H, s, CH$_2$); 2.41 (2H, s, CH$_2$); 4.61 (1H, s, =CH); 6.41 (2H, br. s, NH$_2$); 6.82 (1H, d, ^3J = 8, C$_6$H$_3$); 7.81 (1H, d, ^4J = 2, C$_6$H$_3$); 7.91 (1H, dd, ^3J = 8, ^4J = 2, C$_6$H$_3$); 8.24 (1H, br. s, NH)
3f	1635; 3400, 3300, 3220	1.01 (6H, s, 2CH$_3$); 2.16 (2H, s, CH$_2$); 2.36 (2H, s, CH$_2$); 3.76 (2H, br. s, NH$_2$); 5.07 (1H, s, =CH); 6.92 (1H, s, C$_6$H$_2$); 7.14 (1H, s, C$_6$H$_2$); 7.56 (1H, br. s, NH)
5a	1630; 3300, 3220, 3100	0.98 (3H, s, CH$_3$); 1.07 (3H, s, CH$_3$); 2.11 (2H, s, CH$_2$); 2.56 (2H, s, CH$_2$); 5.93 (1H, s, CH); 6.16 (1H, br. s, NH); 6.53-6.97 (7H, m, C$_6$H$_4$, C$_6$H$_3$); 8.78 (1H, br. s, NH)
5b	1633; 3300, 3200, 3100	0.93 (3H, s, CH$_3$); 0.98 (3H, s, CH$_3$); 1.96 (1H, d, ^2J = 16, CH); 2.13 (1H, d, ^2J = 16, CH); 2.51 (2H, s, CH$_2$); 5.73 (1H, d, ^3J = 5, CH); 6.04 (1H, d, ^3J = 5, NH); 6.53-7.02 (6H, m, C$_6$H$_4$, C$_5$H$_4$N); 7.41 (1H, m, C$_5$H$_4$N); 8.33 (1H, m, C$_5$H$_4$N); 8.71 (1H, br. s, NH)
5c	1628; 33320, 3210, 100	1.01 (3H, s, CH$_3$); 1.08 (3H, s, CH$_3$); 2.12 (1H, d, ^2J = 18, CH); 2.26 (1H, d, ^2J = 18, CH); 2.61 (2H, s, CH$_2$); 5.76 (1H, d, ^3J = 5, CH); 6.26 (1H, d, ^3J = 5, NH); 6.56-7.47 (6H, m, C$_6$H$_4$, C$_5$H$_3$N); 8.21 (1H, dd, ^3J = 5, ^4J = 1.5, C$_5$H$_4$N); 8.37 (1H, d, ^4J = 1.5, C$_5$H$_4$N); 8.92 (1H, br. s, NH)
5d	1630; 3300, 3190, 3100	0.95 (3H, s, CH$_3$); 1.03 (3H, s, CH$_3$); 2.07 (1H, d, ^2J = 16, CH); 2.19 (1H, d, ^2J = 16, CH); 2.58 (2H, s, CH$_2$); 5.64 (1H, d, ^3J = 5, CH); 6.27 (1H, d, ^3J = 5, NH); 6.47-6.98 (6H, m, C$_6$H$_4$, C$_5$H$_4$N); 8.27 (2H, m, C$_5$H$_4$N); 8.78 (1H, br. s, NH)
5e	1710, 1630; 3320, 3180, 3080	1.01 (3H, s, CH$_3$); 1.12 (3H, s, CH$_3$); 2.12 (1H, d, ^2J = 17, CH); 2.23 (1H, d, ^2J = 17, CH); 2.65 (2H, m, CH$_2$); 3.81 (3H, s, OCH$_3$); 5.67 (1H, d, ^3J = 5, CH); 5.92 (2H, s, O-CH$_2$-O); 6.56 (4H, m, 2C$_6$H$_3$); 6.92 (1H, d, ^3J = 5, NH); 7.24 (1H, dd, ^3J = 8, ^4J = 2, C$_6$H$_3$); 7.74 (1H, d, ^3J = 2, C$_6$H$_3$); 9.05 (1H, br. s, NH)
5f	1710, 1635; 3300, 3200	1.01 (3H, s, CH$_3$); 1.11 (3H, s, CH$_3$); 2.18 (2H, s, CH$_2$); 2.63 (2H, s, CH$_2$); 3.78 (3H, s, OCH$_3$); 5.76 (1H, d, ^3J = 5, CH); 6.47 (1H, d, ^3J = 5, NH); 6.66-7.02 (4H, m, 2C$_6$H$_3$); 7.34 (1H, dd, ^3J = 8, ^4J = 1.5, C$_6$H$_3$); 7.69 (1H, d, ^4J = 1.5, C$_6$H$_3$); 9.09 (1H, br. s, NH)
5g	1705,1638; 3330, 3100-3050	0.99 (3H, s, CH$_3$); 1.07 (3H, s, CH$_3$); 2.02 (1H, d, ^2J = 18, CH); 2.18 (1H, d, ^2J = 18, CH); 2.59 (2H, s, CH$_2$); 3.78 (3H, s, OCH$_3$); 5.83 (1H, d, ^3J = 5, CH); 6.65 (1H, d, ^3J = 8, C$_6$H$_3$); 6.96 (1H, d, ^3J = 5, NH); 7.03-7.53 (3H, m, C$_5$H$_4$N, C$_6$H$_3$); 7.77 (1H, d, ^4J = 2, C$_6$H$_3$); 8.26-8.41 (2H, m, C$_5$H$_4$N); 9.12 (1H, br. s, NH)
5h	1706, 1640; 3300, 3080	1.01 (3H, s, CH$_3$); 1.12 (3H, s, CH$_3$); 2.14 (1H, d, ^2J = 16, CH); 2.21 (1H, d, ^2J = 16, CH); 2.55 (2H, m, CH$_2$); 3.76 (3H, s, OCH$_3$); 5.76 (1H, d, ^3J = 5, CH); 6.68 (1H, d, ^3J = 8, C$_6$H$_3$); 6.96 (3H, m, ^3J = 5, C$_5$H$_4$N, NH); 7.32 (1H, dd, ^3J = 8, ^4J = 2, C$_6$H$_3$); 7.41 (1H, d, ^4J = 2, C$_6$H$_3$); 8.41 (2H, m, ^3J = 5, C$_5$H$_4$N); 9.12 (1H, br. s, NH)

TABLE 2 (continued)

1	2	3
5i	1640, 1630; 3350, 3200, 3080	0.94 (3H, s, CH_3); 1.08 (3H, s, CH_3); 2.07 (1H, d, ${}^2J = 18$, CH); 2.18 (1H, d, ${}^2J = 18$, CH); 2.61 (2H, s, CH_2); 5.88 (1H, d, ${}^3J = 5$, CH); 6.72 (1H, d, ${}^3J = 8$, C_6H_3); 7.18 (3H, m, C_6H_3, NH); 7.57 (6H, m, C_6H_5, C_6H_4); 7.97-8.07 (3H, m, C_6H_4); 9.08 (1H, br. s, NH)
5j	1645, 1630; 3320, 3180, 3070	0.99 (3H, s, CH_3); 1.02 (3H, s, CH_3); 2.03 (1H, d, ${}^2J = 16$, CH); 2.15 (1H, d, ${}^2J = 16$, CH); 2.53 (2H, s, CH_2); 5.71 (1H, br. s, CH); 6.66 (1H, d, ${}^3J = 8$, C_6H_3); 7.07-7.56 (9H, m, C_5H_4N, C_6H_4, NH); 8.31 (3H, m, C_6H_4, C_6H_3); 8.98 (1H, br. s, NH)
5k	1645, 1635; 3300, 3200, 3090	1.01 (3H, s, CH_3); 1.03 (3H, s, CH_3); 2.06 (1H, d, ${}^2J = 17$, CH); 2.18 (1H, d, ${}^2J = 17$, CH); 2.53 (2H, s, CH_2); 5.96 (1H, d, ${}^3J = 2$, CH); 6.74-7.08 (5H, m, C_6H_3, C_4H_3S); 7.04 (1H, d, ${}^3J = 5$, NH); 7.59 (6H, m, C_6H_5, C_6H_3); 8.99 (1H, br. s, NH)
5l	1640, 1630; 3320, 3200, 3100	0.93 (3H, s, CH_3); 1.03 (3H, s, CH_3); 2.11 (1H, d, ${}^2J = 17$, CH); 2.26 (1H, d, ${}^2J = 17$, CH); 2.53 (2H, s, CH_2); 5.77 (3H, m, C_4H_3O); 6.14 (1H, m, C_6H_3); 6.71 (1H, d, ${}^3J = 5$, CH); 7.08 (2H, m, C_6H_3, NH); 7.36-7.69 (6H, m, C_6H_5, C_6H_3); 8.98 (1H, br. s, NH)
5m	1630; 3350, 3220	0.93 (3H, s, CH_3); 1.08 (3H, s, CH_3); 2.04 (1H, d, ${}^2J = 18$, CH); 2.17 (1H, d, ${}^2J = 18$, CH); 2.61 (2H, s, CH_2); 5.71 (1H, d, ${}^3J = 5$, CH); 6.58-7.27 (8H, m, C_6H_4, C_6H_3, NH); 8.99 (1H, br. s, NH)
5n	1632; 3320, 3200, 3090	0.96 (3H, s, CH_3); 1.07 (3H, s, CH_3); 2.05 (1H, d, ${}^2J = 16$, CH); 2.17 (1H, d, ${}^2J = 16$, CH); 2.61 (2H, s, CH_2); 5.72 (1H, d, ${}^3J = 5$, CH); 6.64-7.29 (8H, m, C_6H_4, C_6H_3, NH); 9.04 (1H, d, ${}^3J = 5$, NH)
5o	1630, 3300, 3210, 3100	1.01 (3H, s, CH_3); 1.05 (3H, s, CH_3); 2.04 (1H, d, ${}^2J = 16$, CH); 2.19 (1H, d, ${}^2J = 16$, CH); 2.24 (2H, s, CH_2); 5.90 (1H, d, ${}^3J = 5$, CH); 6.73-7.30 (7H, m, C_6H_3, C_4H_3S, NH); 9.00 (1H, br. s, NH)
5p	1630; 3330, 3200, 3100-3050	0.96 (3H, s, CH_3); 1.08 (3H, s, CH_3); 2.04 (1H, d, ${}^2J = 16$, CH); 2.16 (1H, d, ${}^2J = 16$, CH); 2.53 (2H, s, CH_2); 5.73 (2H, m, C_4H_3O, CH); 6.12 (1H, m, C_4H_3O); 6.71-7.38 (5H, m, C_6H_3, C_4H_3O, NH); 8.93 (1H, br. s, NH)
5q	1635; 3350, 3240, 3100-3050	1.01 (3H, s, CH_3); 1.06 (3H, s, CH_3); 2.05 (1H, d, ${}^2J = 18$, CH); 2.18 (1H, d, ${}^2J = 18$, CH); 2.52 (2H, s, CH_2); 5.99 (1H, d, ${}^3J = 6$, CH); 6.79-7.58 (6H, m, C_6H_3, C_4H_3S, NH); 7.97 (1H, d, ${}^4J = 2$, C_6H_3); 9.17 (1H, br. s, NH)
5r	1631; 3330, 3200, 3100-3050	0.92 (3H, s, CH_3); 1.03 (3H, s, CH_3); 2.02 (1H, d, ${}^2J = 18$, CH); 2.16 (1H, d, ${}^2J = 18$, CH); 2.52 (2H, s, CH_2); 5.81 (2H, m, C_4H_3N, CH); 6.12 (1H, m, C_4H_3O); 6.82 (1H, d, ${}^3J = 8$, C_6H_3); 7.43-7.58 (2H, m, C_4H_3O, NH); 7.62 (1H, dd, ${}^3J = 8$, ${}^4J = 2$, C_6H_3); 7.97 (1H, d, ${}^4J = 2$, C_6H_3); 9.12 (1H, br. s, NH)
5s	1630; 3300, 3210, 3100	1.05 (3H, s, CH_3); 1.12 (3H, s, CH_3); 2.23 (2H, s, CH_2); 2.52 (2H, s, CH_2); 3.67 (3H, s, OCH_3); 3.81 (3H, s, OCH_3); 4.96 (1H, br. s, NH); 5.72 (1H, br. s, CH); 6.62 (3H, m, C_6H_3); 7.18 (1H, s, C_6H_2); 7.43 (1H, s, C_6H_2); 8.43 (1H, br. s, NH)
5t	1632; 3340, 3200, 3100	1.12 (3H, s, CH_3); 1.15 (3H, s, CH_3); 2.25 (2H, s, CH_2); 2.61 (2H, s, CH_2); 5.87 (1H, s, CH); 6.47-6.83 (4H, m, C_6H_3, NH); 6.85 (1H, s, C_6H_2); 7.47 (1H, s, C_6H_2); 8.61 (1H, br. s, NH)
5u	1630; 3320, 3220, 3100	1.06 (3H, s, CH_3); 1.07 (3H, s, CH_3); 2.21 (2H, s, CH_2); 2.61 (2H, s, CH_2); 5.78 (1H, d, ${}^3J = 5$, CH); 6.66 (1H, d, ${}^3J = 5$, NH); 6.84 (1H, s, C_6H_2); 7.27 (1H, s, C_6H_2); 7.28-7.45 (2H, m, C_5H_4N); 8.36 (2H, m, C_5H_4N); 9.06 (1H, br. s, NH)

11-(2-Pyridyl)- (5b), 11-(3-Pyridyl)- (5c), 11-(4-Pyridyl)- (5d), 7-Methoxycarbonyl-11-(3-pyridyl)- (5g), 7-Methoxycarbonyl-11-(4-pyridyl)- (5h), 7-Benzoyl-11-(4-pyridyl)- (5j), 7,8-Dichloro-11-(4-pyridyl)- (5u) 3,3-dimethyl-1,2,3,4,10,11-hexahydro-5H-dibenzo[*b,e*][1,4]diazepin-1-ones. The corresponding enaminone **3** (3 mmol) and pyridine carbaldehyde (3 mmol) were boiled in ethanol (40 ml) in the presence of conc. H_2SO_4 (0.15 ml) for 3 h. Ethanol (25-30 ml) was distilled off on a rotary evaporator, water (40 ml) was added, and the mixture was neutralized with a concentrated aqueous solution of $NaHCO_3$. The precipitate was filtered out and recrystallized from 2-propanol.

11-(3,5-Difluorophenyl)- (5a), 7-Methoxycarbonyl-11-(3,4-methylenedioxyphenyl)- (5e), 7-Methoxycarbonyl-11-(3,5-difluorophenyl)- (5f), 7,8-Dichloro-11-(3,4-dimethoxyphenyl)- (5s), 7,8-Dichloro-11-(3,5-difluoro)- (5t) 3,3-dimethyl-1,2,3,4,10,11-hexahydro-5H-dibenzo[*b,e*][1,4]diazepin-1-ones. Enaminone **3** (3 mmol) and the corresponding aldehyde **4** (2.5 mmol) were boiled in ethanol (30 ml) in the presence of 2 drops of conc. H_2SO_4 for 2.5 h; half the volume of the ethanol was driven off on a rotary evaporator and the mixture was placed in a refrigerator for 24 hours. Water (1-2 ml) was added as needed. The precipitate was filtered out and recrystallized from ethanol (compounds **5a,s**), 2-propanol (compounds **5e,f**), or THF (compound **5t**).

3,3-Dimethyl-7-nitro-11-(2-thienyl)-1,2,3,4,10,11-hexahydro-5H-dibenzo[*b,e*][1,4]diazepin-1-one (5q). Enaminone **3e** (3 mmol) and thiophene-2-carbaldehyde **4j** (3 mmol) were boiled in ethanol (30 ml) in the presence of conc. H_2SO_4 (0.15 ml) for 4 h. The mixture was poured into crushed ice and then the precipitate of dibenzodiazepine was filtered out and recrystallized from 2-propanol.

7-Benzoyl- (5l), 7-Trifluoromethyl- (5p), 7-Nitro- (5r) 3,3-dimethyl-11-(2-furyl)-1,2,3,4,10,11-hexahydro-5H-dibenzo[*b,e*][1,4]diazepin-1-ones. A mixture of enaminone **3** (2 mmol), furfural (2 mmol), glacial CH_3COOH (0.3 ml), and piperidine (0.4 ml) were boiled for 3 h in ethanol (30 ml). The mixture was cooled and poured into crushed ice. The precipitate was filtered out and recrystallized from toluene.

7-Benzoyl-11-(3-nitrophenyl)- (5i), 7-Benzoyl-11-(2-thienyl)- (5k), 11-(4-Chlorophenyl)-7-trifluoromethyl- (5m), 7-Trifluoromethyl-11-(4-fluorophenyl)- (5n), 11-(2-Thienyl)-7-trifluoromethyl- (5o) 3,3-dimethyl-1,2,3,4,10,11-hexahydro-5H-dibenzo[*b,e*][1,4]diazepin-1-ones. A mixture of enaminone **3c,d** (2 mmol) and the corresponding aldehyde **4** (2 mmol) were boiled for 3 h in ethanol (30 ml) in the presence of conc. H_2SO_4 (0.15 ml). The mixture was cooled and poured into crushed ice. The precipitate of dibenzodiazepine was filtered out and recrystallized from toluene.

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