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CONVENIENT CONSTRUCTION OF HEXAHYDROBENZO-[*b*]FURAN SKELETON CONTAINING HETEROATOMS. CHOICE OF Mn(III)- AND Ce(IV)-BASED RADICAL CYCLIZATION†

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Abstract - Hexahydrobenzo[*b*]furan derivatives were efficiently synthesized by the radical cyclization of 1-arylcyclohexenes, 1-phenylcycloheptene, and 1,1-diarylethenes with barbituric acid derivatives or 5,5-dimethyl-1,3-cyclohexanedione (dimedone) using manganese(III) acetate or cerium(IV) ammonium nitrate (CAN).

INTRODUCTION

Polycyclic compounds containing the hexahydrobenzo[*b*]furan skeleton widely exist in nature and it is known that some have significant biologically active characteristics. For example, morphine and codeine are well-known as a plant alkaloid,[1] norpinguisone, pinuisone, and pinguisenol are antifungal agents isolated from some bryophyta,[2] piperenone shows a distinct antifeeding activity isolated from plant leaves,[3] and (+)-phyllanthocin is an antitumor inhibitor isolated from a plant root.[4] Barbituric acid derivatives have widespread use as a medical hypnotic drug, and are also present in nature as

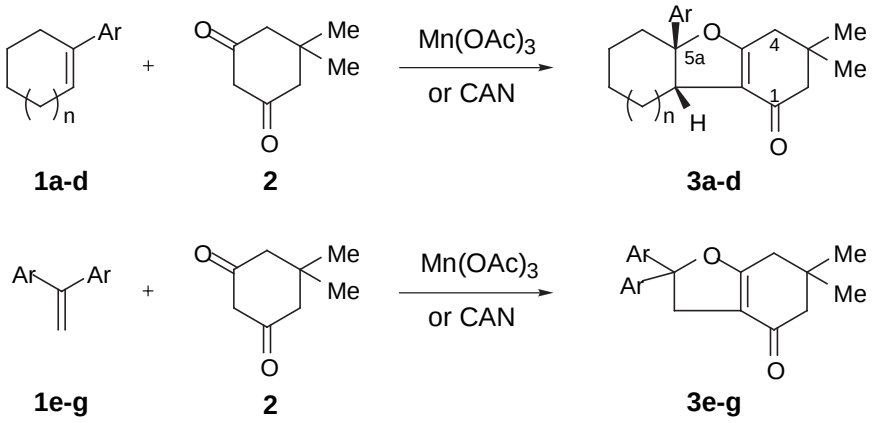
†Dedicated to Professor Shô Itô, Professor of Tokushima Bunri University, Japan, on his 77th birthday.

pyrimidine derivatives in nucleic acids.[5] Further viewpoint of developing biologically active novel agents and medical supplies, a convenient one-pot synthesis of hexahydrobenzo[*b*]furans with a fused pyrimidine ring was desired. With respect to this work, it was reported that the manganese(III)-based radical cyclization of alkenes with cyclic 1,3-dicarbonyl compounds gave cyclic peroxides,[6] hexahydrobenzo[*b*]furans,[7] 4,6-dioxo-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan,[8] and 4-oxo-6-thia-2,3,4,5,6,7-hexahydrobenzo[*b*]furan.[9] The reaction was quite useful in some cases, however, it appeared that the yields should be improved in some cases. Recently, Nair *et al*. showed that cerium(IV) ammonium nitrate (CAN) was a superior oxidant to the commonly used manganese(III) acetate for the radical cyclization.[10] With these backgrounds, we embarked on the synthesis of the hexahydrobenzo[*b*]furans fused pyrimidine ring using the Mn(III)- or Ce(IV)-based one-pot radical cyclization.

RESULTS AND DISCUSSION

Reaction of Alkenes (1a-g) with Dimedone (2). In order to confirm the usefulness of using manganese(III) acetate or CAN for the synthesis of the hexahydrobenzo[*b*]furans, 1-arylcyclohexenes (**1a-c**), 1-phenylcycloheptene (**1d**), and 1,1-diarylethenes (**1e-g**) were allowed to react with dimedone (**2**) according to the literature[7,10] and our modified method.[11] As a result, the corresponding hexahydrobenzo[*b*]furans (**3a-g**) were obtained in high yields (Scheme 1 and Table 1). It was proved that both

Scheme 1



a : Ar = Ph, n = 1
b : Ar = 4-Cl-C_6H_4, n = 1
c : Ar = 4-Me-C_6H_4, n = 1
d : Ar = Ph, n = 2

e : Ar = Ph
f : Ar = 4-Cl-C_6H_4
g : Ar = 4-Me-C_6H_4

Table 1. Reaction of Alkenes (1a-g) with Dimedone (2) in the Presence of Manganese(III) Acetate or Cerium(IV) Ammonium Nitrate[a]

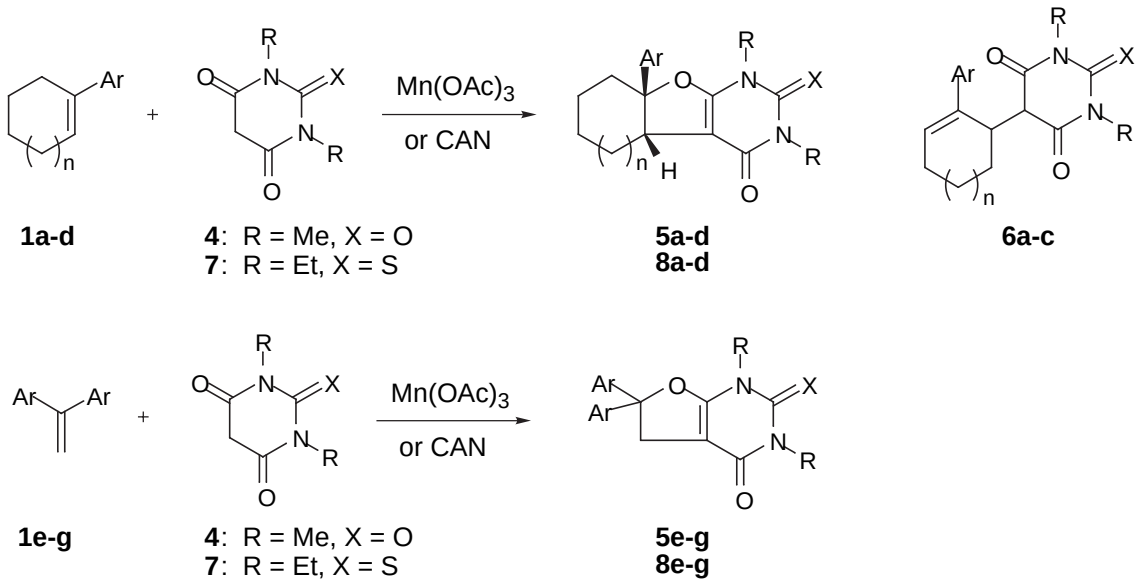
Entry	Alkene	Oxidant	Molar ratio[b]	Time/min	Product (Yield/%)[c]
1	**1a**	Mn(III)	1:2.9:3	3	**3a** (100)
2	**1a**	Ce(IV)	1:1.2:2.5	15	**3a** (97)
3	**1b**	Mn(III)	1:3.1:3	3	**3b** (100)
4	**1b**	Ce(IV)	1:1.2:2.4	15	**3b** (98)
5	**1c**	Mn(III)	1:3:3	3	**3c** (97)
6	**1c**	Ce(IV)	1:1.2:2.4	15	**3c** (91)
7	**1d**	Mn(III)	1:3:3.1	3	**3d** (93)
8	**1d**	Ce(IV)	1:1.2:2.5	15	**3d** (98)
9	**1e**	Mn(III)	1:3.2:3.2	3	**3e** (94)[d]
10	**1e**	Ce(IV)	1:1.3:2.6	15	**3e** (81)[d]
11	**1f**	Mn(III)	1:3:3.1	3	**3f** (94)[e]
12	**1f**	Ce(IV)	1:2:4	15	**3f** (35)[e]
13	**1g**	Mn(III)	1:3:3	3	**3g** (97)[f]
14	**1g**	Ce(IV)	1:1.2:2.4	15	**3g** (87)[f]

[a] The reaction of the alkene (**1**) with manganese(III) acetate was carried out in boiling acetic acid (10 mL), while the reaction of **1** with CAN was conducted in methanol (15 mL) at 0 °C. [b] The molar ratio of alkene (**1**):dimedone (**2**):oxidant. [c] Isolated yield based on the amount of the alkene (**1**) used. [d] Benzophenone (5%) was also isolated. [e] 4,4'-Dichlorobenzophenone (4%) was also isolated. [f] 4,4'-Dimethylbenzophenone (2%) was also isolated.

oxidants were very efficient, but the cyclization using manganese(III) acetate was slightly superior compared to using CAN. This contrasts with the result reported by Nair *et al.*[10] The stereochemistry of the aryl group at 5a and the H-9a hydrogen in the ring junction of **3b** was determined by an NOE experiment. That is, it was apparent that the cyclohexane fused benzofuran ring had a *cis*-configuration since the irradiation of the aromatic proton that appeared at δ 7.30 (4H, s) resulted in a 3.2% increase in the triplet at δ 3.37 (1H, J = 5.2). Moreover, the simple MOPAC calculation of **3a** and **3d** also supported the fact that the formation energy of the cis hexahydrobenzo[*b*]furan was much lower than that of the trans one.[12] Therefore, it seemed that the stereochemistry of the hexahydrobenzo[*b*]furans (**3a-d**) was the *cis*-configuration. This stereochemistry result was in accord with that of Nair *et al.*[10]

Reaction of Alkenes (1a-g) with Barbituric Acid Derivatives (4,7). On the basis of these results,

Scheme 2



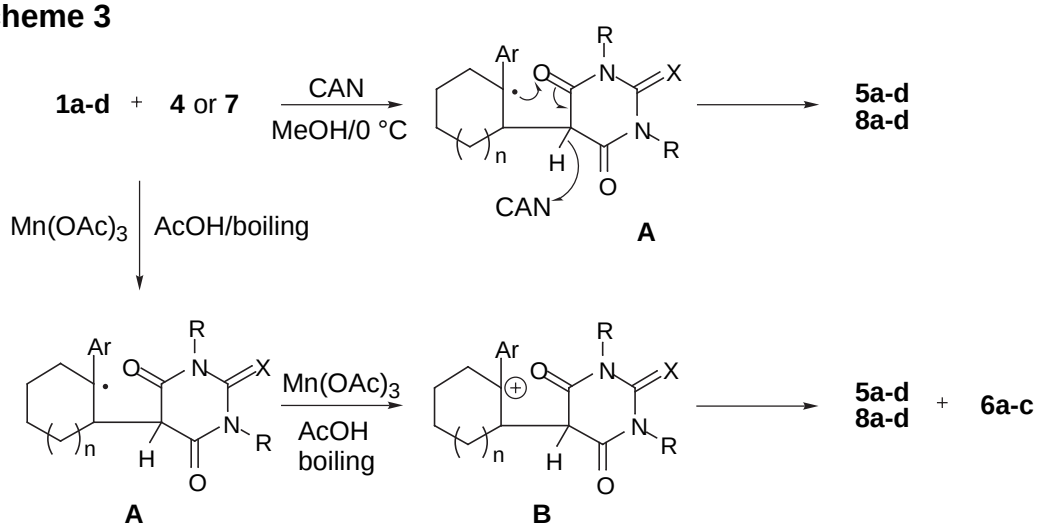
barbituric acid derivatives (**4**,**7**) instead of **2** were allowed to react with the alkenes (**1a-g**) in the presence of manganese(III) acetate in glacial acetic acid or CAN in methanol. The cyclization using CAN gave the corresponding hexahydrobenzo[*b*]furans (**5a-g**, **8a-g**) in good yields as the sole product, while the Mn(III)-based reaction afforded the same cyclization products (**5a-f**, **8a-f**) together with substitution products (**6a-c**) (Scheme 2 and Table 2). Especially, the reaction of 1-(4-methylphenyl)cyclohexene (**1c**) with **4** in the presence of manganese(III) acetate mainly gave the substitution product (**6c**) (Table 2, Entry 9). In addition, the Mn(III)-based reaction of 1,1-bis(4-methylphenyl)ethene (**1g**) with **4** or **7** yielded an intractable mixture and no products were isolated (Table 2, Entries 25 and 27). Therefore, the ability of CAN was quite superior to that of manganese(III) acetate with respect to the synthesis of the hexahydrobenzo[*b*]furans fused pyrimidine skeleton. The predominance for the cyclization using CAN probably depends on the ability to oxidize the tertiary carbon radical (**A**) formed during the reaction (Scheme 3).[13] That is, CAN (Ce(IV) + e^- → Ce(III), E_0 = 1.61 V) is a much stronger oxidant than manganese(III) acetate (Mn(III) + e^- → Mn(II), E_0 = 1.51 V).[14] Therefore, CAN was able to abstract a hydrogen in the intermediate radical (**A**) at 0 °C and the concerted cyclization gave the products (**5a-d** or **8a-d**) as the sole product, however, manganese(III) acetate allowed the oxidation of **A** under reflux conditions to give the corresponding tertiary cation (**B**)[15] which should be transformed by deprotonation to cyclic products (**5** or **8**) and a substitution product (**6**). It was deduced that the stereochemisty of **5a-d** and **8a-d** was also the same as

Table 2. Reaction of Alkenes (1a-g) with Barbituric Acid Derivatives (4,7) in the Presence of Manganese(III) Acetate or Cerium(IV) Ammonium Nitrate[a]

Entry	Alkene	Barbituric acid	Oxidant	Molar ratio[b]	Time/min	Product (Yield/%)[c]	
1	**1a**	**4**	Mn(III)	1:4:4	3	**5a** (68)	**6a** (23)
2	**1a**	**4**	Ce(IV)	1:1.2:2.5	15	**5a** (78)	
3	**1a**	**7**	Mn(III)	1:4:4.1	3	**8a** (82)	
4	**1a**	**7**	Ce(IV)	1:1.2:2.4	15	**8a** (97)	
5	**1b**	**4**	Mn(III)	1:4:4.1	3	**5b** (57)	**6b** (30)
6	**1b**	**4**	Ce(IV)	1:1.2:2.5	15	**5b** (81)	
7	**1b**	**7**	Mn(III)	1:4:4	3	**8b** (83)	
8	**1b**	**7**	Ce(IV)	1:1.2:2.5	15	**8b** (91)	
9	**1c**	**4**	Mn(III)	1:4:4	3	**5c** (4)	**6c** (75)
10	**1c**	**4**	Ce(IV)	1:1.2:2.4	15	**5c** (73)	
11	**1c**	**7**	Mn(III)	1:4:4.1	3	**8c** (66)	
12	**1c**	**7**	Ce(IV)	1:1.2:2.4	15	**8c** (85)	
13	**1d**	**4**	Mn(III)	1:4.1:4.1	3	**5d** (82)	
14	**1d**	**4**	Ce(IV)	1:1.2:2.4	15	**5d** (81)	
15	**1d**	**7**	Mn(III)	1:4:4	3	**8d** (83)	
16	**1d**	**7**	Ce(IV)	1:1.2:2.4	15	**8d** (87)	
17	**1e**	**4**	Mn(III)	1:3.1:3.2	3	**5e** (65)[d]	
18	**1e**	**4**	Ce(IV)	1:1.2:2.4	15	**5e** (76)[d]	
19	**1e**	**7**	Mn(III)	1:3:3.1	3	**8e** (73)[d]	
20	**1e**	**7**	Ce(IV)	1:1.2:2.4	15	**8e** (79)[d]	
21	**1f**	**4**	Mn(III)	1:3:3	3	**5f** (67)[e]	
22	**1f**	**4**	Ce(IV)	1:2:4.1	15	**5f** (81)[e]	
23	**1f**	**7**	Mn(III)	1:3:3	3	**8f** (72)[e]	
24	**1f**	**7**	Ce(IV)	1:2:4	15	**8f** (73)[e]	
25[f]	**1g**	**4**	Mn(III)	1:3:3	3		
26	**1g**	**4**	Ce(IV)	1:1.2:2.4	15	**5g** (63)[g]	
27[f]	**1g**	**7**	Mn(III)	1:3:3	3		
28	**1g**	**7**	Ce(IV)	1:1.2:2.4	15	**8g** (68)[g]	

[a] The reaction of the alkene (**1**) with manganese(III) acetate was carried out in boiling acetic acid (10 mL), while the reaction of **1** with CAN was conducted in methanol (15 mL) at 0 °C. [b] The molar ratio of alkene (**1**):barbituric acid derivatives (**4**,**7**):oxidant. [c] Isolated yield based on the amount of the alkene (**1**) used. [d] Benzophenone (4-6%) was also isolated. [e] 4,4'-Dichlorobenzophenone (2-10%) was also isolated. [f] The reaction gave an intractable mixture and the corresponding products were not isolated. [g] 4,4'-Dimethylbenzophenone (2-6%) was also isolated.

Scheme 3



that of **3a-d** since the NOE experiments of **5b** and **8b** revealed similar results to that of **3b** (see EXPERIMENTAL).

CONCLUSION

Nineteen new hexahydrobenzo[*b*]furans (**3b-g**, **5a-d**,**f**,**g**, **8a-g**) were synthesized in one-pot by the convenient Mn(III)- or Ce(IV)-based radical cyclization of alkenes (**1a-g**) with dimedone (**2**) and barbituric acid derivatives (**4** and **7**). In the reaction with the barbituric acid derivatives (**4** and **7**), the ability of CAN was demonstrated by the radical cyclization. Photo-induced benzannulation of these hexahydrobenzo[*b*]furans obtained by the radical cyclization gave polycyclic naphthalene derivatives in high yields.[16]

EXPERIMENTAL

Measurements. All of the NMR spectra were recorded on a JNM EX400 FT NMR spectrometer at 400 MHz for ^{1}H and at 100 MHz for ^{13}C, a JNM-AL 300 FT NMR spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, or a JNM EX90 FT NMR spectrometer at 90 MHz for ^{1}H and at 22.5 MHz for ^{13}C with tetramethylsilane as the internal standard. Chemical shifts are shown in δ and coupling constants in Hz. The IR spectra were measured using either a Paragon 1000 FT IR spectrophotometer or a JASCO A-102 IR spectrophotometer. The IR spectral data are expressed in cm^{-1}. The MS spectra were measured on either a Shimadzu GCMS QP2000GF or a JMS-BU20 mass spectrometer. All of the melting points were determined with a Yanaco MP-J3 micromelting-point apparatus and are uncorrected. Elemental analyses were performed by the Center of Instrumental Analysis, Kumamoto University, Kumamoto, Japan.

Materials. Manganese(II) acetate tetrahydrate, $Mn(OAc)_2 \cdot 4H_2O$, and cerium(IV) ammonium nitrate were purchased from Wako Pure Chemical Ind., Ltd., and were used as received. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to the method described in the literature.[17] The 1-arylcycloalkenes (**1a-d**) and 1,1-diarylethenes (**1e-g**) were prepared by dehydration of the corresponding alcohols which were synthesized by the Grignard reaction of cycloalkanones and substituted acetophenones with arylmagnesium bromides. Dimedone (**2**) and 1,3-dimethylbarbituric acid (**4**) were purchased from Tokyo-Kasei Co., Ltd., and 1,3-diethyl-2-thiobarbituric acid (**7**) was purchased from Aldrich Chemical Co., Inc., and were used as received.

Manganese(III)-Based Radical Cyclization of Alkenes (1a-g) with Dimedone (2) or Barbituric Acid Derivatives (4,7). To a boiled solution of the alkene (**1**) (1 mmol) in glacial acetic acid (10 mL), dimedone (**2**) or the barbituric acid derivative (**4** or **7**) and then manganese(III) acetate dihydrate were added. The solution was heated under reflux with stirring. The reaction time and the molar ratio of **1**:**2**,**4** or **7**:manganese(III) acetate are shown in Tables 1 and 2. The dark-brown color of Mn(III) disappeared within 3 min. Water (60 mL) was added, and the aqueous mixture was extracted with dichloromethane (3 x 20 mL). The combined extracts were successively washed with water and a saturated aqueous solution of sodium hydrogencarbonate, and then dried over anhydrous magnesium sulfate. The dried extract was filtered and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10 or Merck Kieselgel $60F_{254}$) using chloroform or ether-hexane (5:5-8:2 v/v) as the developing solvent. Analytical samples were further purified by recrystallization from the appropriate solvent mentioned below except for the liquid products.

Cerium(IV)-Based Radical Cyclization of Alkenes (1a-g) with Dimedone (2) or Barbituric Acid Derivatives (4,7). To an ice-cooled solution of the alkene (**1**) (1 mmol) and dimedone (**2**) or the barbituric acid derivative (**4** or **7**) in methanol (5 mL), a solution of CAN in methanol (10 mL) was added dropwise. The solution was stirred at 0 °C. The reaction time and the molar ratio of **1**:**2**,**4** or **7**:CAN are shown in Tables 1 and 2. The reddish brown color of CAN disappeared within 15 min. Water (60 mL) was added, and the mixture was then extracted with dichloromethane (3 x 20 mL). The combined extract was washed with brine, and then dried over anhydrous magnesium sulfate. The extract was filtered and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10 or Merck Kieselgel $60F_{254}$) using chloroform or diethyl ether-hexane (5:5-8:2 v/v) as the developing solvent. Analytical samples were further purified by recrystallization from the appropriate solvent mentioned below except for the liquid products.

3,3-Dimethyl-5a-phenyl-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one (3a): Light yellow liquid[10]; IR ($CHCl_3$) 1627 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.39-7.21 (5H, m, arom H), 3.44 (1H, tt, *J* = 5.1, 1.5 Hz, CH), 2.34 (2H, d, *J* = 1.5 Hz, H-4), 2.18 (2H, s, H-2), 2.04-1.90 (4H, m, 2 x CH_2), 1.63-1.45 (4H, m, 2 x CH_2), 1.13 (3H, s, CH_3), 1.07 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.8 (C=O), 175.3 (=C-O), 146.3 (arom C), 128.3 (2C), 127.3, 124.2 (2C) (arom CH), 115.1 (C-9b), 94.0 (C-5a), 51.2 (CH_2), 44.3 (CH), 37.9 (CH_2), 34.1 (C-3), 33.9 (CH_2), 29.2, 28.2 (CH_3), 24.1, 18.0, 17.9 (CH_2); MS *m/z* (rel intensity) 296 (M^+, 18), 234 (11), 174 (22), 145 (42), 130 (39), 105 (82), 91 (52), 85 (76), 83 (100), 77 (41).

(5a*S,9a*S**)-5a-(4-Chlorophenyl)-3,3-dimethyl-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one (3b):** Colorless microcrystals (from CH_2Cl_2-hexane), mp 105-108 °C; IR ($CHCl_3$) 1628 (C=O); ^{1}H

NMR (300 MHz, $CDCl_3$) 7.30 (4H, s, arom H), 3.37 (1H, tt, *J* = 5.1, 1.5 Hz, CH), 2.38 (2H, d, *J* = 1.5 Hz, H-4), 2.19 (2H, s, H-2), 2.04-1.85 (4H, m, 2 x CH_2), 1.64-1.44 (4H, m, 2 x CH_2), 1.13 (3H, s, CH_3), 1.08 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.8 (C=O), 175.2 (=C-O), 144.9, 133.1 (arom C), 128.4 (2C), 125.7 (2C) (arom CH), 115.1 (C-9b), 93.5 (C-5a), 51.1 (CH_2), 44.3 (CH), 37.9 (CH_2), 34.1 (C-3), 33.9 (CH_2), 29.1, 28.1 (CH_3), 24.2, 18.0, 17.9 (CH_2); MS *m/z* (rel intensity) 330 (M^+, 100), 166 (59), 164 (93), 129 (71), 83 (69). Anal. Calcd for $C_{20}H_{23}O_2Cl$: C, 72.61; H, 7.01. Found: C, 72.44; H, 7.18. HRMS Found: *m/z* 330.1397. Calcd for $C_{20}H_{23}O_2Cl$: M, 330.1387.

5a-(4-Methylphenyl)-3,3-dimethyl-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one (3c): Colorless plates (from CH_2Cl_2-hexane), mp 92-94 °C; IR ($CHCl_3$) 1625 (C=O); ^1H NMR (300 MHz, $CDCl_3$) 7.28-7.13 (4H, m, arom H), 3.43 (1H, tt, *J* = 5.1, 1.5 Hz, CH), 2.37 (2H, d, *J* = 1.5 Hz, H-4), 2.33 (3H, s, CH_3), 2.19 (2H, s, H-2), 2.06-1.84 (4H, m, 2 x CH_2), 1.65-1.41 (4H, m, 2 x CH_2), 1.13 (3H, s, CH_3), 1.08 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.9 (C=O), 175.4 (=C-O), 143.3, 137.1 (arom C), 129.0 (2C), 124.2 (2C) (arom CH), 115.2 (C-9b), 94.1 (C-5a), 51.2 (CH_2), 44.3 (CH), 38.0 (CH_2), 34.1 (C-3), 33.9 (CH_2), 29.2, 28.2 (CH_3), 24.2 (CH_2), 21.0 (CH_3), 18.1, 18.0 (CH_2); MS *m/z* (rel intensity) 310 (M^+, 81), 158 (30), 144 (100), 129 (47). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.46; H, 8.35.

3,3-Dimethyl-5a-phenyl-1,2,3,4,5a,7,8,9,10,10a-decahydro-6*H*-cyclohepta[*b*]benzofuran-1-one (3d): Light yellow liquid; IR ($CHCl_3$) 1628 (C=O); ^1H NMR (300 MHz, $CDCl_3$) 7.37-7.20 (5H, m, arom H), 3.59 (1H, ddt, *J* = 2.9, 6.2, 1.7 Hz,CH), 2.40 (2H, d, *J* = 1.7 Hz, H-4), 2.36-1.78 (4H, m, 2 x CH_2), 2.19 (2H, s, H-2), 1.74-1.29 (6H, m, 3 x CH_2), 1.15 (3H, s, CH_3), 1.08 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.5 (C=O), 174.1 (=C-O), 148.1 (arom C), 128.3 (2C), 127.1, 123.7 (2C) (arom CH), 113.8 (C-10b), 98.1 (C-5a), 51.2 (CH_2), 50.6 (CH), 40.8, 37.8 (CH_2), 33.9 (C-3), 31.2, 29.3 (CH_2), 29.3, 28.3 (CH_3), 26.3, 24.2 (CH_2); MS *m/z* (rel intensity) 310 (M^+, 100), 219 (39), 165 (37), 91 (39), 83 (36). HRMS Found: *m/z* 310.1950. Calcd for $C_{21}H_{26}O_2$: M, 310.1933.

6,6-Dimethyl-2,2-diphenyl-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one (3e): Colorless needles (from CH_2Cl_2-hexane), mp 121-122 °C; IR ($CHCl_3$) 1630 (C=O); ^1H NMR (90 MHz, $CDCl_3$) 7.67-6.90 (10H, m, arom H), 3.56 (2H, t, *J* = 1.7 Hz, H-3), 2.39 (2H, t, *J* = 1.7 Hz, H-7), 2.20 (2H, s, H-5), 1.05 (6H, s, 2 x CH_3); ^{13}C NMR (22.5 MHz, $CDCl_3$) 193.9 (C=O), 174.0 (C-7a), 144.1 (2C) (arom C), 128.0 (4C), 127.3 (2C), 125.2 (4C) (arom CH), 110.8 (C-3a), 95.2 (C-2), 50.5 (C-3), 40.1 (C-5), 37.5 (C-7), 33.7 (C-6), 28.2 (2 x CH_3); MS *m/z* (rel intensity) 318 (M^+, 100), 300 (47), 220 (50), 192 (49), 191 (97), 165 (48), 83 (93). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.75; H, 6.87.

2,2-Bis(4-chlorophenyl)-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one (3f): Colorless microcrystals (from CH_2Cl_2-hexane), mp 99-101 °C; IR ($CHCl_3$) 1634 (C=O); ^1H NMR (300 MHz, $CDCl_3$) 7.32-7.24 (8H, m, arom H), 3.49 (2H, t, *J* = 1.7 Hz, H-3), 2.44 (2H, t, *J* = 1.7 Hz, H-7), 2.25 (2H, s, H-5), 1.12 (6H, s, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.4 (C=O), 174.1 (C-7a), 142.6 (2C), 133.9 (2C) (arom C), 128.7 (4C), 127.0 (4C) (arom CH), 111.2 (C-3a), 94.5 (C-2), 50.9 (C-3), 40.4 (C-5), 37.7 (C-7), 34.2 (C-6), 28.7 (2 x CH_3); MS *m/z* (rel intensity) 386 (M^+, 28), 369 (31), 139 (27), 83 (100). Anal. Calcd for $C_{22}H_{20}O_2Cl_2$: C, 68.23; H, 5.20. Found: C, 68.47; H, 5.24.

2,2-Bis(4-methylphenyl)-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one (3g): Colorless needles (from CH_2Cl_2-hexane), mp 124-125 °C; IR ($CHCl_3$) 1631 (C=O); ^1H NMR (300 MHz, $CDCl_3$) 7.24-7.10 (8H, m, arom H), 3.53 (2H, t, *J* = 1.7 Hz, H-3), 2.41 (2H, t, *J* = 1.7 Hz, H-7), 2.30 (6H, s, 2 x CH_3), 2.22 (2H, s, H-5), 1.10 (6H, s, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 194.5 (C=O), 174.6 (C-7a),

141.7 (2C), 137.4 (2C) (arom C), 129.0 (4C), 125.6 (4C) (arom CH), 111.3 (C-3a), 95.7 (C-2), 50.9 (C-3), 40.4 (C-5), 37.8 (C-7), 34.1 (C-6), 28.7 (2 x CH_3), 21.0 (2 x CH_3); MS *m/z* (rel intensity) 346 (M^+, 59), 328 (94), 219 (100), 83 (61). Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.32; H, 7.64.

2,4-Dimethyl-5a-phenyl-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1,3-dione (5a): Colorless liquid; IR ($CHCl_3$) 1702, 1658 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.44-7.28 (5H, m, arom H), 3.72 (1H, t, *J* = 5.0 Hz, CH), 3.44 (3H, s, NCH_3), 3.29 (3H, s, NCH_3), 2.17-1.91 (4H, m, 2 x CH_2), 1.66-1.51 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 161.0, 160.4 (C=O), 151.7 (C-4a), 144.3 (arom C), 128.5 (2C), 128.0, 124.3 (2C) (arom CH), 96.9 (C-9b), 89.7 (C-5a), 44.6 (CH), 34.3 (CH_2), 29.5, 27.8 (NCH_3), 24.3, 18.4, 17.9 (CH_2); MS *m/z* (rel intensity) 312 (M^+, 100), 182 (80), 157 (88), 156 (88), 130 (42). HRMS Found: *m/z* 312.1477. Calcd for $C_{18}H_{20}N_2O_3$: M, 312.1474.

(5a*S,9a*S**)-5a-(4-Chlorophenyl)-2,4-dimethyl-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1,3-dione (5b):** Colorless microcrystals (from ether), mp 158-160 °C; IR ($CHCl_3$) 1703, 1658 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.38-7.32 (4H, m, arom H), 3.67 (1H, t, *J* = 5.0 Hz, CH), 3.45 (3H, s, NCH_3), 3.29 (3H, s, NCH_3), 2.17-1.89 (4H, m, 2 x CH_2), 1.66-1.51 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 160.8, 160.3 (C=O), 151.7 (C-4a), 142.9, 133.8 (arom C), 128.7 (2C), 125.9 (2C) (arom CH), 96.3 (C-9b), 89.5 (C-5a), 44.6 (CH), 34.2 (CH_2), 29.5, 27.8 (NCH_3), 24.2, 18.3, 17.9 (CH_2); MS *m/z* (rel intensity) 346 (M^+, 69), 190 (77), 182 (100), 157 (77). Anal. Calcd for $C_{18}H_{19}N_2O_3Cl$: C, 62.34; H, 5.52; N, 8.08. Found: C, 62.62; H, 5.78; N, 8.20. HRMS Found: *m/z* 346.1093. Calcd for $C_{18}H_{19}N_2O_3Cl$: M, 346.1084.

The irradiation of the top of the aromatic proton that appeared at δ 7.38-7.32 resulted in a 3.3% increase in the triplet at δ 3.67. This was supported by the fact that the stereochemistry of the aryl group and the H-9a hydrogen involved the *syn* configuration.

5a-(4-Methylphenyl)-2,4-dimethyl-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1,3-dione (5c): Colorless microcrystals (from diethyl ether), mp 102-104 °C; IR ($CHCl_3$) 1702, 1656 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.32-7.16 (4H, m, arom H), 3.71 (1H, t, *J* = 5.0 Hz, CH), 3.43 (3H, s, NCH_3), 3.28 (3H, s, NCH_3), 2.33 (3H, s, CH_3), 2.17-1.88 (4H, m, 2 x CH_2), 1.64-1.49 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 161.0, 160.4 (C=O), 151.7 (C-4a), 141.2, 137.8 (arom C), 129.2 (2C), 124.4 (2C) (arom CH), 96.9 (C-9b), 89.6 (C-5a), 44.6 (CH), 34.2 (CH_2), 29.4, 27.7 (NCH_3), 24.3 (CH_2), 21.0 (CH_3), 18.5, 18.1 (CH_2); MS *m/z* (rel intensity) 326 (M^+, 88), 170 (100), 157 (72), 144 (61). Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.14; H, 7.04; N, 8.82. HRMS Found: *m/z* 326.1667. Calcd for $C_{19}H_{22}N_2O_3$: M, 326.1630.

2,4-Dimethyl-5a-phenyl-2,4-diaza-1,2,3,4,5a,7,8,9,10,10a-decahydro-6*H*-cyclohepta[*b*]benzofuran-1,3-dione (5d): Colorless microcrystals (from ether), mp 188-190 °C; IR ($CHCl_3$) 1702, 1664 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41-7.24 (5H, m, arom H), 3.86 (1H, dd, *J* = 2.9, 6.9 Hz, CH), 3.47 (3H, s, NCH_3), 3.27 (3H, s, NCH_3), 2.28-1.96 (4H, m, 2 x CH_2), 1.74-1.41 (6H, m, 3 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 160.0, 159.6 (C=O), 151.7 (C-4a), 146.1 (arom C), 128.5 (2C), 127.7, 123.8 (2C) (arom CH), 100.9 (C-10b), 88.9 (C-5a), 50.7 (CH), 40.8, 31.0, 29.4 (CH_2), 29.4, 27.7 (NCH_3), 26.3, 23.9 (CH_2); MS *m/z* (rel intensity) 326 (M^+, 100), 170 (45). Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.14; H, 6.92; N, 8.59. HRMS Found: *m/z* 326.1641. Calcd for $C_{19}H_{22}N_2O_3$: M, 326.1630.

5,7-Dimethyl-2,2-diphenyl-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4,6-dione (5e):

Colorless needles (from CH_2Cl_2-hexane), mp 190-191 °C (lit.,[8] mp 190-191 °C); IR ($CHCl_3$) 1705, 1663 (C=O); ^{1}H NMR (90 MHz, $CDCl_3$) 7.50-7.15 (10H, m, arom H), 3.80 (2H, s, CH_2), 3.45 (3H, s, NCH_3), 3.29 (3H, s, NCH_3); ^{13}C NMR (22.5 MHz, $CDCl_3$) 159.9, 159.8 (C=O), 151.3 (C-7a), 142.6 (2C) (arom C), 128.3 (4C), 128.0 (2C), 125.4 (4C) (arom CH), 97.3 (C-3a), 85.6 (C-2), 40.3 (CH_2), 29.3, 27.7 (NCH_3); MS *m/z* (rel intensity) 334 (M^+, 100), 319 (43), 220 (66), 205 (67), 192 (49), 191 (67), 178 (42).

2,2-Bis(4-chlorodiphenyl)-5,7-dimethyl-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4,6-dione (5f): Colorless needles (from CH_2Cl_2-hexane), mp 182-184 °C; IR ($CHCl_3$) 1708, 1666 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.36-7.26 (8H, m, arom H), 3.75 (2H, s, CH_2), 3.47 (3H, s, NCH_3), 3.31 (3H, s, NCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 160.0, 159.9 (C=O), 151.5 (C-7a), 141.0 (2C), 134.7 (2C) (arom C), 128.9 (4C), 127.1 (4C) (arom CH), 96.5 (C-3a), 85.7 (C-2), 40.5 (CH_2), 29.7, 28.1 (NCH_3); MS *m/z* (rel intensity) 402 (M^+, 100), 273 (40), 225 (57), 189 (48), 176 (43), 94 (42). Anal. Calcd for $C_{20}H_{16}N_2O_3Cl_2$: C, 59.57; H, 4.00; N, 6.95. Found: C, 59.39; H, 4.04; N, 6.87.

2,2-Bis(4-methyldiphenyl)-5,7-dimethyl-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4,6-dione (5g): Colorless microcrystals (from ether), mp 120-122 °C; IR ($CHCl_3$) 1704, 1661 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.25-7.15 (8H, m, arom H), 3.77 (2H, s, CH_2), 3.45 (3H, s, NCH_3), 3.31 (3H, s, NCH_3), 2.34 (6H, s, 2 x CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 160.3, 160.2 (C=O), 151.7 (C-7a), 140.1 (2C), 138.3 (2C) (arom C), 129.2 (4C), 125.7 (4C) (arom CH), 97.9 (C-3a), 86.0 (C-2), 40.6 (CH_2), 29.7, 28.0 (NCH_3), 21.0 (2 x CH_3); MS *m/z* (rel intensity) 362 (M^+, 100), 347 (83), 233 (49). Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 73.01; H, 6.36; N, 7.80. HRMS Found: *m/z* 362.1624. Calcd for $C_{22}H_{22}N_2O_3$: M, 362.1630.

5-(2-Phenyl-2-cyclohexenyl)-1,3-dimethylbarbituric Acid (6a): Yellow liquid; IR ($CHCl_3$) 1678 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.32-7.17 (5H, m, arom H), 5.97-5.93 (1H, m, alkenic H), 3.87-3.79 (1H, m, CH), 3.48 (1H, d, *J* = 3.0 Hz, H-5), 3.15 (3H, s, NCH_3), 3.09 (3H, s, NCH_3), 2.22-2.16 (2H, m, CH_2), 2.03-1.56 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 168.3, 167.8, 151.2 (C=O), 141.4 (alkenic CH), 138.0 (arom C), 130.3 (alkenic C), 128.3 (2C), 127.2, 126.9 (2C) (arom CH), 51.5 (CH), 41.5 (C-5), 28.2 (2 x NCH_3), 27.8, 25.5, 21.0 (CH_2); MS *m/z* (rel intensity) 335 (M^++Na, 28), 157 (99), 156 (100). FABHRMS ($CHCl_3$-NBA-NaI) Found: *m/z* 335.1354. Calcd for $C_{18}H_{20}N_2O_3Na$: M, 335.1371.

5-[2-(4-Chlorophenyl)-2-cyclohexenyl]-1,3-dimethylbarbituric Acid (6b): Yellow liquid; IR ($CHCl_3$) 1681 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.30-7.21 (4H, m, arom H), 5.98-5.94 (1H, m, alkenic H), 3.79-3.71 (1H, m, CH), 3.49 (1H, d, *J* = 3.0 Hz, H-5), 3.21 (3H, s, NCH_3), 3.14 (3H, s, NCH_3), 2.21-2.14 (2H, m, CH_2), 1.96-1.57 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 168.4, 167.2, 151.3 (C=O), 139.9 (alkenic C), 137.1, 132.9 (arom C), 130.6 (alkenic CH), 128.5 (2C), 128.3 (2C) (arom CH), 51.0 (CH), 41.1 (C-5), 28.4, 28.2 (NCH_3), 26.7, 25.4, 20.7 (CH_2); MS *m/z* (rel intensity) 369 (M^++Na, 18), 190 (35), 157 (100). FABHRMS ($CHCl_3$-NBA-NaI) Found: *m/z* 369.0963. Calcd for $C_{18}H_{19}N_2O_3ClNa$: M, 369.0982.

5-[2-(4-Methylphenyl)-2-cyclohexenyl]-1,3-dimethylbarbituric Acid (6c): Yellow liquid; IR ($CHCl_3$) 1678 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) 7.13-7.06 (4H, m, arom H), 5.93-5.90 (1H, m, alkenic CH), 3.83-3.75 (1H, m, CH), 3.47 (1H, d, *J* = 2.8 Hz, H-5), 3.14 (3H, s, NCH_3), 3.07 (3H, s, NCH_3), 2.29 (3H, s, CH_3), 2.22-2.12 (2H, m, CH_2), 2.00-1.54 (4H, m, 2 x CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) 168.3, 167.8, 151.2 (C=O), 138.5 (alkenic C), 137.8, 136.8 (arom C), 129.5 (alkenic CH), 128.9 (2C), 126.8 (2C) (arom CH), 51.4 (CH), 41.7 (C-5), 28.2 (2 x NCH_3), 27.8, 25.5 (CH_2), 21.0 (CH_3 and

CH_2); MS *m/z* (rel intensity) 349 (M^++Na, 100), 170 (91), 157 (87). FABHRMS ($CHCl_3$-NBA-NaI) Found: *m/z* 349.1519. Calcd for $C_{19}H_{22}N_2O_3Na$: M, 349.1528.

2,4-Diethyl-5a-phenyl-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one-3-thione (8a): Colorless needles (from ether), mp 134-135 °C; IR ($CHCl_3$) 1679, 1652 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.45-7.28 (5H, m, arom H), 4.66-4.43 (4H, m, 2 x $NC\underline{H}_2CH_3$), 3.78 (1H, t, *J* = 4.6 Hz, CH), 2.23-1.88 (4H, m, 2 x CH_2), 1.67-1.48 (4H, m, 2 x CH_2), 1.40 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.6 (C=S), 160.5 (C=O), 158.6 (C-4a), 143.9 (arom C), 128.6 (2C), 128.1, 124.3 (2C) (arom CH), 96.6 (C-9b), 94.4 (C-5a), 44.7 (CH), 44.5, 43.1 ($N\underline{C}H_2CH_3$), 34.1, 23.4, 18.1, 17.7 (CH_2), 12.8, 11.7 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 356 (M^+, 100), 226 (51), 201 (61), 156 (64). Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79; N, 7.86. Found: C, 67.55; H, 7.08; N, 7.75. HRMS Found: *m/z* 356.1564. Calcd for $C_{20}H_{24}N_2O_2S$: M, 356.1558.

(5a*S,9a*S**)-5a-(4-Chlorophenyl)-2,4-diethyl-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one-3-thione (8b):** Colorless microcrystals (from ether), mp 160-161 °C; IR ($CHCl_3$) 1680, 1652 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.37 (4H, s, arom H), 4.66-4.42 (4H, m, 2 x $NC\underline{H}_2CH_3$), 3.73 (1H, t, *J* = 4.6 Hz, CH), 2.25-1.87 (4H, m, 2 x CH_2), 1.67-1.47 (4H, m, 2 x CH_2), 1.39 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.5 (C=S), 160.4 (C=O), 158.5 (C-4a), 142.4, 134.0 (arom C), 128.8 (2C), 125.9 (2C) (arom CH), 96.0 (C-9b), 94.3 (C-5a), 44.7 (CH), 44.5, 43.2 ($N\underline{C}H_2CH_3$), 34.0, 23.4, 18.1, 17.7 (CH_2), 12.8, 11.7 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 390 (M^+, 100), 226 (91). Anal. Calcd for $C_{20}H_{23}N_2O_2ClS$: C, 61.45; H, 5.93; N, 7.17. Found: C, 61.67; H, 6.20; N, 7.07. HRMS Found: *m/z* 390.1170. Calcd for $C_{20}H_{23}N_2O_2ClS$: M, 390.1169.

The irradiation of the aromatic proton that appeared at δ 7.37 resulted in a 3.1% increase in the triplet at δ 3.73. It was apparent that the stereochemistry of the aryl group and the H-9a hydrogen also involved the syn configuration.

2,4-Diethyl-5a-(4-methylphenyl)-2,4-diaza-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzofuran-1-one-3-thione (8c): Colorless microcrystals (from ether), mp 131-133 °C; IR ($CHCl_3$) 1679, 1651 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.34-7.18 (4H, m, arom H), 4.64-4.42 (4H, m, 2 x $NC\underline{H}_2CH_3$), 3.77 (1H, t, *J* = 4.6 Hz, CH), 2.35 (3H, s, CH_3), 2.26-1.87 (4H, m, 2 x CH_2), 1.67-1.48 (4H, m, 2 x CH_2), 1.39 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.5 (C=S), 160.6 (C=O), 158.7 (C-4a), 140.8, 138.0 (arom C), 129.2 (2C), 124.4 (2C) (arom CH), 96.7 (C-9b), 94.5 (C-5a), 44.7 (CH), 44.4, 43.1 ($N\underline{C}H_2CH_3$), 34.0, 23.5 (CH_2), 21.0 (CH_3), 18.3, 17.9 (CH_2), 12.8, 11.7 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 370 (M^+, 78), 201 (68), 170 (100), 144 (44). Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.08; H, 7.07; N, 7.56 Found: C, 68.26; H, 7.09; N, 7.56. HRMS Found: *m/z* 370.1700. Calcd for $C_{21}H_{26}N_2O_2S$: M, 370.1715.

2,4-Diethyl-5a-phenyl-2,4-diaza-1,2,3,4,5a,7,8,9,10,10a-decahydrocyclohepta[*b*]benzofuran-1-one-3-thione (8d): Colorless microcrystals (from ether), mp 104-105 °C; IR ($CHCl_3$) 1679, 1652 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.43-7.25 (5H, m, arom H), 4.68-4.44 (4H, m, 2 x $NC\underline{H}_2CH_3$), 3.91 (1H, dd, *J* = 6.3, 2.3 Hz, CH), 2.35-1.98 (4H, m, 2 x CH_2), 1.78-1.45 (6H, m, 3 x CH_2), 1.43 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.27 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.5 (C=S), 159.3 (C=O), 158.2 (C-4a), 146.0 (arom C), 128.6 (2C), 127.8, 123.7 (2C) (arom CH), 100.6 (C-10b), 94.0 (C-5a), 50.7 (CH), 44.5, 43.1 ($N\underline{C}H_2CH_3$), 41.1, 30.9, 29.0, 26.3, 24.0 (CH_2), 12.8, 11.7 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 370 (M^+, 100), 170 (80), 129 (43), 91 (49). Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.08;

H, 7.07; N, 7.56. Found: C, 67.91; H, 7.29; N, 7.40. HRMS Found: *m/z* 370.1731. Calcd for $C_{21}H_{26}N_2O_2S$: M, 370.1715.

5,7-Diethyl-2,2-diphenyl-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one-6-thione (8e): Colorless cubes (from CH_2Cl_2-hexane), mp 109-111 °C; IR ($CHCl_3$) 1682, 1655 (C=O, C=S); ^{1}H NMR (400 MHz, $CDCl_3$) 7.38-7.32 (10H, m, arom H), 4.58 (2H, q, *J* = 6.8 Hz, $NC\underline{H}_2CH_3$), 4.55 (2H, q, *J* = 6.8 Hz, $NC\underline{H}_2CH_3$), 3.84 (2H, s, CH_2), 1.40 (3H, t, *J* = 6.8 Hz, $NCH_2C\underline{H}_3$), 1.29 (3H, t, *J* = 6.8 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) 175.6 (C=S), 159.9 (C=O), 158.3 (C-7a), 142.7 (2C) (arom C), 128.6 (4C), 128.4 (2C), 125.6 (4C) (arom CH), 97.5 (C-3a), 91.0 (C-2), 44.8, 43.3 ($N\underline{C}H_2CH_3$), 40.6 (CH_2), 12.8, 11.6 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 378 (M^+, 100), 220 (90), 191 (43). Anal. Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.81; H, 5.86; N, 7.40. Found: C, 70.08; H, 5.99; N, 7.42.

2,2-Bis(4-chlorophenyl)-5,7-diethyl-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one-6-thione (8f): Colorless microcrystals (from ether), mp 150-152 °C; IR ($CHCl_3$) 1685, 1655 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.38-7.27 (8H, m, arom H), 4.58 (2H, q, *J* = 7.0 Hz, $NC\underline{H}_2CH_3$), 4.53 (2H, q, *J* = 7.0 Hz, $NC\underline{H}_2CH_3$), 3.77 (2H, s, CH_2), 1.38 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.6 (C=S), 159.6 (C=O), 158.3 (C-7a), 140.8 (2C), 134.8 (2C) (arom C), 129.0 (4C), 127.1 (4C) (arom CH), 96.4 (C-3a), 90.8 (C-2), 44.8, 43.5 ($N\underline{C}H_2CH_3$), 40.5 (CH_2), 12.9, 11.6 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 446 (M^+, 100), 288 (33), 225 (24), 189 (21). Anal. Calcd for $C_{22}H_{20}N_2O_2Cl_2S$: C, 59.06; H, 4.51; N, 6.26. Found: C, 58.79; H, 4.61; N, 6.37. HRMS Found: *m/z* 446.0618. Calcd for $C_{22}H_{20}N_2O_2Cl_2S$: M, 446.0622.

5,7-Diethyl-2,2-bis(4-methylphenyl)-5,7-diaza-2,3,4,5,6,7-hexahydrobenzo[*b*]furan-4-one-6-thione (8g): Light yellow liquid; IR ($CHCl_3$) 1679, 1653 (C=O, C=S); ^{1}H NMR (300 MHz, $CDCl_3$) 7.25-7.15 (8H, m, arom H), 4.56 (2H, q, *J* = 7.0 Hz, $NC\underline{H}_2CH_3$), 4.53 (2H, q, *J* = 7.0 Hz, $NC\underline{H}_2CH_3$), 3.78 (2H, s, CH_2), 2.34 (6H, s, 2 x CH_3), 1.38 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 1.28 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) 175.6 (C=S), 160.0 (C=O), 158.6 (C-7a), 139.9 (2C), 138.4 (2C) (arom C), 129.3 (4C), 125.7 (4C) (arom CH), 97.9 (C-3a), 91.2 (C-2), 44.8, 43.4 ($N\underline{C}H_2CH_3$), 40.6 (CH_2), 21.0 (2C) (CH_3), 12.8, 11.7 ($NCH_2\underline{C}H_3$); MS *m/z* (rel intensity) 406 (M^+, 100), 248 (76). Anal. Calcd for $C_{24}H_{26}N_2O_2S$: C, 70.90; H, 6.45; N, 6.89. Found: C, 70.95; H, 6.61; N, 6.76. HRMS Found: *m/z* 406.1703. Calcd for $C_{24}H_{26}N_2O_2S$: M, 406.1715.

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