SIMPLE ROUTE TO AZABICYCLIC PEROXIDES FROM TETRAMIC ACID DERIVATIVES USING MANGANESE(III)-BASED MOLECULAR OXYGEN TRAPPING REACTION†[1]

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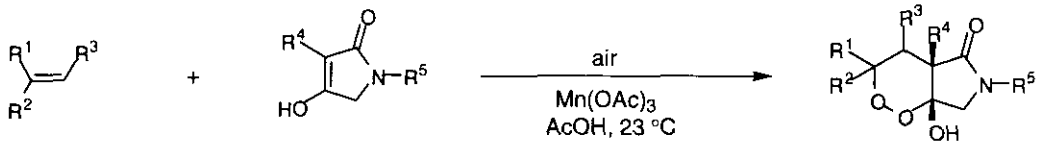
Abstract - A simple one-step synthesis of azabicyclic peroxides was achieved by the manganese(III)-mediated oxidative formal [2+2+2] cycloaddition. The reaction of alkenes (**1**) with pyrrolidinediones (**2**) was carried out with manganese(III) acetate in acetic acid at 23 °C under a dry air stream to give 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-ones (**3**) in good to quantitative yields. Similar reactions at elevated temperature gave 3-ethyl-2,4-pyrrolidinediones (**4**) and/or 3-ethenyl-2,4-pyrrolidinediones (**5**) in good yields.

INTRODUCTION

Nitrogen heterocycles widely occur in nature and as structural subunits in many families of alkaloids, and possess wide-ranging biological and pharmaceutical activities. Tetramic acids, 2,4-pyrrolidinediones, are a particularly important sub-group, and are well known for their potent antibiotic, antiviral, and antifungal as well as cytotoxic activities,[2] *e.g.*, tenuazonic acid,[3] ikarugamycin,[4] streptolydigin,[5] magnesidin,[6] malonomicin,[7] erythroskyrine,[8] and tirandamycin.[9] Naturally occurring bicyclic peroxides are also known as a plant growth regulator isolated from *Eucalyptus grandis*[10] and as antimalarial peroxides yingzhaous C from *Artabotrys uncinatus*,[11] and arteannuin from *Artemisia annua*.[12] For the construction of much more biologically effective compounds, we used tetramic acid

†Dedicated to the Memory of Professor Emeritus Hitoshi Takeshita, Kyushu University.

Scheme 1



1a-n **2a-j** **3**

1a : $R^1 = R^2 = Ph$, $R^3 = H$
1b : $R^1 = R^2 = 4\text{-}MeC_6H_4$, $R^3 = H$
1c : $R^1 = R^2 = 4\text{-}MeOC_6H_4$, $R^3 = H$
1d : $R^1 = R^2 = 4\text{-}ClC_6H_4$, $R^3 = H$
1e : $R^1 = R^2 = 4\text{-}FC_6H_4$, $R^3 = H$
1f : $R^1 = Me$, $R^2 = Ph$, $R^3 = H$
1g : $R^1 = R^2 = Me$, $R^3 = H$
1h : $R^1 = R^2 = Et$, $R^3 = H$
1i : $R^1, R^3 = -(CH_2)_6-$, $R^2 = H$
1j : $R^1 = Ph$, $R^2 = 4\text{-}ClC_6H_4$, $R^3 = H$
1k : $R^1 = Ph$, $R^2 = 4\text{-}BrC_6H_4$, $R^3 = H$
1l : $R^1 = Ph$, $R^2 = 4\text{-}MeOC_6H_4$, $R^3 = H$
1m : $R^1 = Me$, $R^2 = 4\text{-}ClC_6H_4$, $R^3 = H$
1n : $R^1 = 4\text{-}ClC_6H_4$, $R^2 = 4\text{-}BrC_6H_4$, $R^3 = H$

2a : $R^4 = CO_2Et$, $R^5 = Bn$
2b : $R^4 = CO_2Me$, $R^5 = Bn$
2c : $R^4 = CO_2Et$, $R^5 = Me$
2d : $R^4 = CO_2Et$, $R^5 = Et$
2e : $R^4 = CO_2Et$, $R^5 = Bu$
2f : $R^4 = CO_2Et$, $R^5 = {}^iBu$
2g : $R^4 = CO_2Et$, $R^5 = H$
2h : $R^4 = CO_2Me$, $R^5 = H$
2i : $R^4 = CN$, $R^5 = Bn$
2j : $R^4 = CN$, $R^5 = Bu$
2k : $R^4 = H$, $R^5 = Bn$

derivatives during bicyclic peroxide synthesis with manganese(III) acetate.[13] The tetramic acid is a tautomer of 2,4-pyrrolidinedione, which is a cyclic 1,3-dicarbonyl compound,[14] and it could be an effective candidate to form carbon radicals during the manganese(III) acetate oxidation.[15] In connection with our previous study, we achieved the synthesis of bicyclic peroxides containing both a 1,2-dioxane ring and a lactam ring during the manganese(III)-based formal [2+2+2] cycloaddition of molecular oxygen and alkenes with 2,3-pyrrolidinediones bearing an electron-withdrawing substitutent, *e.g.*, a carbonyl or a cyano group, at the C-4 position.[16] These approaches prompted us to use tetramic acid derivatives in the manganese(III)-based formal [2+2+2] cycloaddition to synthesize azabicyclic peroxides, as it was expected to permit a simple, short, efficient, and versatile route. In this paper we delineated a novel one-pot synthesis of 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-ones and related compounds by the manganese(III)-based reaction of readily available alkenes with 2,4-pyrrolidinediones both at 23 °C under air and at reflux temperature under an argon atmosphere. We also established the mechanism for the formation of these compounds.

RESULTS AND DISCUSSION

Preparation of 2,4-Pyrrolidinedione Derivatives. The 2,4-pyrrolidinediones used as substrates in our studies were alkyl 2,4-pyrrolidinedione-3-carboxylates (**2a-h**), 3-cyano-2,4-pyrrolidinediones (**2i,j**), and 1-benzyl-2,4-pyrrolidinedione (**2k**). The pyrrolidinedione derivatives (**2a-h**) were prepared by

condensation of *N*-substituted glycinates with malonic acid monoesters followed by cyclization in the presence of sodium alkoxides.[17] 3-Cyano-2,4-pyrrolidinediones (**2i,j**) were also prepared by the same method as mentioned above. However in these cases, cyanoacetic acid was used instead of ethyl hydrogen malonate. All of these pyrrolidinediones (**2a-j**) exist in the enol form, i.e., as 4-hydroxy-3-pyrrolin-2-one derivatives except for **2k**. The pyrrolidinedione (**2a**) could be converted into the corresponding dione (**2k**) by brief treatment in boiling water.[17b]

Molecular Oxygen Trapping Reaction of Alkenes (1a-n) with 2,4-Pyrrolidinediones (2a-k) in the Presence of Manganese(III) Acetate at 23°C. A mixture of alkenes (**1a-n**) and 2,4-pyrrolidinedione derivatives (**2a-k**) was oxidized with manganese(III) acetate under a dry air stream to produce the expected azabicyclic peroxides (**3**) (Scheme 1, Table 1). All reactions were carried out at the molar ratio of **1**:**2**:manganese(III) acetate = 1:2:1 except for Entries 7-9 and 29. The best yield of the azabicyclic peroxides (**3**) was achieved in the case of the reaction of **1b** having a methyl group on the aromatic ring with **2a** (Entry 2). Surprisingly, the use of gaseous 2-methylpropene (**1g**) (Entry 7) and 1-benzyl-2,4-pyrroridinedione (**2k**), which is present as the keto form in the solution (Entries 24-29), remarkably shortened the reaction time compared to that of the other ethenes and 2,4-pyrrolidinediones. It was found that the reaction of **1a** with *N*-deprotected 2,4-pyrrolidinedione (**2g**) or (**2h**) decreased the yields of the cyclic peroxide **3** (Entries 20, 21) since the amido hydrogen might be sensitive to the manganese(III) oxidant under these conditions.[18] The introduction of a cyano group at C-3 position of the pyrrolidinedione also gave the corresponding azabicyclic peroxides probably in a similar manner (Entries 22, 23).

Structure Determination of Azabicyclic Peroxide (3ga). The structure of **3ga** was established by spectroscopic methods, elemental analysis, and finally X-Ray crystallography. The ^{1}H NMR spectrum showed the three characteristic pairs of the AX system at δ 4.75 and 4.33 (J = 15.0 Hz), δ 3.57 and 3.14 (J = 10.8 Hz), and δ 2.50 and 2.23 (J = 14.4 Hz) assigned to the methylene protons of the benzyl group, pyrrolinone ring, and dioxane ring, respectively, together with peaks due to a phenyl (δ 7.28), a hydroxyl (δ 5.06 which disappeared upon deuteration), an ethoxyl (δ 4.11 and 1.11), and two methyl groups (δ 1.26 and 1.22). In the ^{13}C NMR spectrum, ester and amide carbonyl carbons appeared at δ 170.4 and 167.8, and three characteristic sp^3 quaternary carbons were observed at δ 100.2, 77.6, and 56.4, which were assigned to the C-1, C-4, and C-6 carbons, respectively. Accordingly, the structure of **3ga** was deduced to be 8-benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-dimethyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one based on these spectral data and, in addition, the elemental analysis supported the molecular formula of $C_{18}H_{23}NO_6$. The stereochemistry of the ring junction of C-1 and C-6 has not been determined, however, from the molecular modeling study, it could be assumed that a *cis*-fused bicyclic peroxide was more stable than the *trans*-isomer.[19] In order to corroborate the structure, we grew a

Table 1. Reaction of Alkenes (1a-n) with 2,4-Pyrrolidinediones (2a-k) in the Presence of Manganese(III) Acetate at 23 °C[a]

Entry	Alkene	2,4-Pyrrolidinedione	Molar ratio[b]	Time/h	Product (Yield/%)[c]
1	**1a**	**2a**	1:2:1	14	**3aa** (93)
2	**1b**	**2a**	1:2:1	14	**3ba** (98)
3	**1c**	**2a**	1:2:1	12	**3ca** (67)
4	**1d**	**2a**	1:2:1	12	**3da** (89)
5	**1e**	**2a**	1:2:1	14	**3ea** (88)
6	**1f**	**2a**	1:2:1	12	**3fa** (76)
7	**1g**	**2a**	Excess:2:1[d]	5	**3ga** (77)[e]
8	**1h**	**2a**	3:1:1	12	**3ha** (58)[e]
9	**1i**	**2a**	3:1:1	16	**3ia** (24)[e]
10	**1j**	**2a**	1:2:1	12	**3ja** (85)
11	**1k**	**2a**	1:2:1	12	**3ka** (89)
12	**1l**	**2a**	1:2:1	12	**3la** (69)
13	**1m**	**2a**	1:2:1	12	**3ma** (86)
14	**1n**	**2a**	1:2:1	12	**3na** (95)
15	**1a**	**2b**	1:2:1	12	**3ab** (74)
16	**1a**	**2c**	1:2:1	12	**3ac** (88)
17	**1a**	**2d**	1:2:1	12	**3ad** (83)
18	**1a**	**2e**	1:2:1	12	**3ae** (83)
19	**1a**	**2f**	1:2:1	12	**3af** (79)
20	**1a**	**2g**	1:2:1	12	**3ag** (73)
21	**1a**	**2h**	1:2:1	14	**3ah** (75)
22	**1a**	**2i**	1:2:1	12	**3ai** (84)
23	**1a**	**2j**	1:2:1	5	**3aj** (88)
24	**1a**	**2k**	1:2:1	3	**3ak** (70)
25	**1b**	**2k**	1:2:1	0.5	**3bk** (80)
26	**1c**	**2k**	1:2:1	0.3	**3ck** (70)
27	**1d**	**2k**	1:2:1	1.4	**3dk** (66)
28	**1e**	**2k**	1:2:1	1	**3ek** (67)
29	**1g**	**2k**	Excess:2:1[d]	1	**3gk** (51)[f]

[a] The reaction was carried out in acetic acid (30 mL) under a dry air stream. [b] The molar ratio is **1**:**2**:manganese(III) acetate. [c] Isolated yield based on the amount of the alkene (**1**) used except for Entries 7-9 and 29. [d] 2-Methylpropene (**1g**) was bubbled into the reaction mixture. [e] Yield based on the amount of **2a** used. [f] Yield based on the amount of **2k** used.

single crystal of pure **3ga** from methanol in the orthorhombic space group *Pbca* with a = 12.125(4), b = 26.971(4), and c = 10.556(2) Å. The crystal structure was solved by direct methods, and **3ga** was found to be exactly the *cis*-fused bicyclic peroxide shown in Figure 1.[13a]

Reaction of Alkenes (1a-e) with 2,4-Pyrrolidinedione (2a) in the Presence of Manganese(III) Acetate at 130 °C. In order to synthesize the 3-aza-6-oxabicyclo[3.3.0]octan-2-one skeleton, a mixture of alkene (**1a**) and 2,4-pyrrolidinedione (**2a**) was treated with manganese(III) acetate in acetic acid *under air at 130 °C*. The reaction product at elevated temperature significantly differed from that *at 23 °C*, and our attempt failed. We only obtained the 3-substituted 2,4- pyrrolidinedione (**4a**)

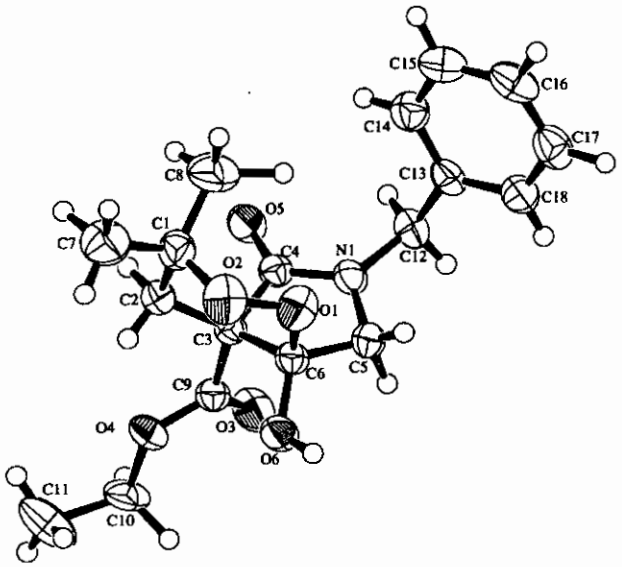
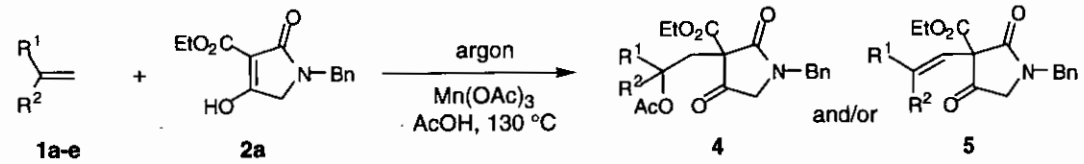


Figure 1. ORTEP Diagram of 3ga

(Scheme 2 and Table 2, Entry 1).[16,18b,c] The same reaction *under an argon atmosphere* improved the yield of **4a** up to 78% (Entry 2). A similar reaction of **1b-e** with **2a** yielded 3-substituted 2,4-pyrrolidinediones (**4d,e**) and/or (**5b,c**) in good yields (Entries 3-6). Accordingly, this reaction appeared to be a convenient route to introduce an ethyl and/or ethenyl group to the 3-position of the 2,4-

Scheme 2



1a-e **2a** **4** **5**

Table 2. Reaction of Alkenes (1a-e) with 2,4-Pyrrolidinedione (2a) in the Presence of Manganese(III) Acetate at 130 °C[a]

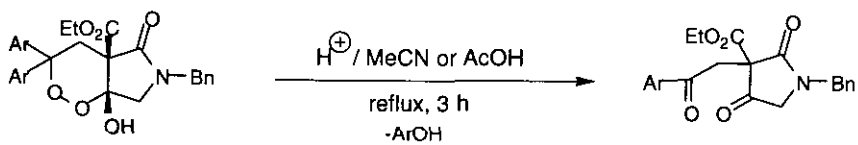
Entry	Alkene	Molar ratio[b]	Time/min	Product (Yield/%)[c]
1[d]	**1a**	1:3:4	5	**4a** (66)
2	**1a**	1:3:4	3	**4a** (78)
3	**1b**	1:3:4	2	**5b** (87)
4	**1c**	1:3:4	1	**5c** (94)
5	**1d**	1:3:4	5	**4d** (75)
6	**1e**	1:3:4	4	**4e** (76)

[a] The reaction was carried out in acetic acid under an argon atmosphere. [b] The molar ratio is **1**:**2a**:manganese(III) acetate. [c] Isolated yield based on the amount of the alkene (1) used. [d] The reaction was conducted under air.

pyrrolidinedione.

Acid-Catalyzed Decomposition of Bicyclic Peroxides (3aa) and (3ca). It was reported that 1,2-dioxan-3-ols were easily decomposed by acid to give furans.[20] When the acid-catalyzed decompositions of **3aa** and **3ca** were carried out, both of these reactions resulted in ketones (**6a**) and (**6c**) by aryl migration (Scheme 3).

Scheme 3

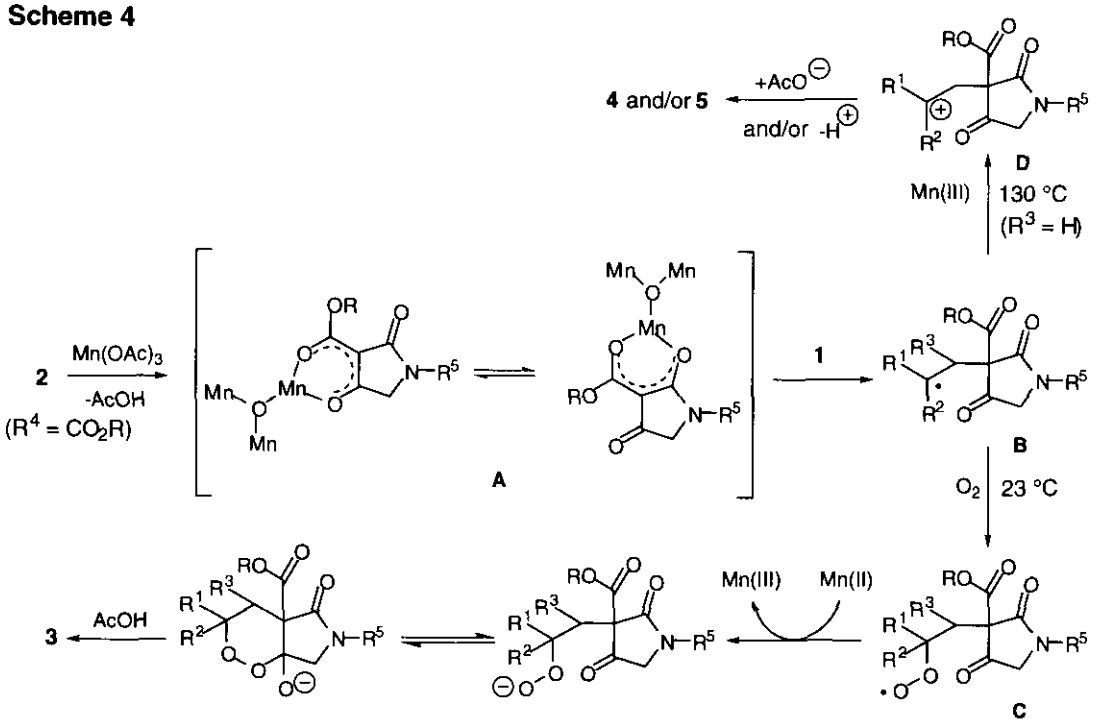


3aa: Ar = Ph
3ca: Ar = 4-MeOC$_6$H$_4$

6a (33%)
6c (55%)

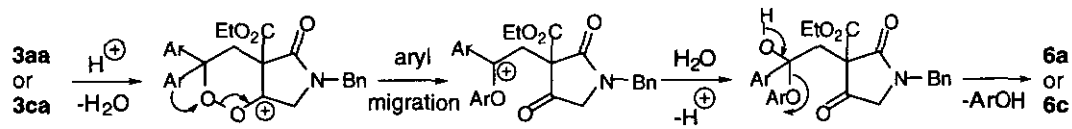
Mechanisms. The formation of **3**, **4** and/or **5** could be explained according to the mechanism outlined in Scheme 4. The Mn(III)-2,4-pyrrolidinedione enolate complex (**A**) should be formed during the first stage similar to the La(III), Sm(III), Eu(III), and Gd(III)-enolate complexes[21] and the subsequent one-electron transfer took place to give the corresponding 2,4-pyrrolidinedione radicals which simultaneously attacked the alkene (**1**) to yield tertiary carbon radicals (**B**) as shown in Scheme 4.[22]
The reaction pathway could depend on the ambient temperature. At 23 °C, the molecular oxygen in

Scheme 4



bubbled air reacted with the carbon radicals (**B**) to produce peroxy radicals (**C**), which were reduced by Mn(II) species followed by cyclization to give the 1,2-dioxan-3-ol (**3**) which was thermodynamically stable *cis*-fused structure.[23] At 130 °C, the Mn(III)-based oxidation of radicals (**B**) to form the carbocation (**D**) could be dominant since the molecular oxygen dissolved in the reaction mixture was neglected.[24] From **D**, the attack of an acetate ion[23c,e,24] and/or a β-proton elimination[24f,26] would yield **4** and/or **5**. The Mn(III) species were regenerated in the reaction at 23 °C, that is, Mn(III) functioned as a catalyst.[23] However, two equivalents of the 2,4-pyrrolidinedione (**2**) against the ethene (**1**) were employed so that the 2,4-pyrrolidinedione itself was also oxidatively decomposed by the manganese(III) acetate. The formation of **6a** and **6c** by the acid-catalyzed decomposition could be responsible for the aryl migration as shown in Scheme 5.[20]

Scheme 5



CONCLUSION

The facile synthesis of 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-ones (**3**) was accomplished by the formal [2+2+2] cycloaddition of alkenes, Mn(III)-2,4-pyrrolidinedione enolate complexes, which were formed *in situ* from manganese(III) acetate and 2,4-pyrrolidinediones (**2**), with molecular oxygen in the air. Although attempts to synthesize 3-aza-6-oxabicyclo[3.3.0]octan-2-ones failed, ethyl, ethenyl, and 2-oxoethyl substituted pyrrolidinediones (**4**, **5**, and **6**) were obtained in good yields.

EXPERIMENTAL SECTION

Measurements. All of the NMR spectra were recorded on a JNM-AL 300 FT NMR spectrometer at 300 MHz for ^{1}H and at 75 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 spectrometer or a JASCO A-102 IR spectrophotometer. The IR spectral data are expressed in cm^{-1}. All of the melting points were determined with a Yanaco micromelting-point apparatus MP-J3 and are uncorrected. Elemental analyses were performed by the Center of Instrumental Analysis, Kumamoto University, and at the Elemental Analysis Center, Faculty of Science, Kyushu University, Fukuoka, Japan.

Materials. Manganese(II) acetate tetrahydrate, $Mn(OAc)_2 \cdot 4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to the method described in the literature.[27] 1,1-Disubstituted ethenes were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides. Other alkenes were purchased from Wako Pure Chemical Ind., Ltd. and used as received. The 2,4-pyrrolidinedione derivatives were prepared according to the references[17] and their physical data are given below.

Ethyl 1-Benzyl-4-hydroxy-3-pyrrolin-2-one-3-carboxylate (2a): colorless microcrystals (from benzene-cyclohexane), mp 148.5-150 °C (lit.,[17b] mp 148.5-150 °C); IR (KBr) 3700-3200 (OH), 1706,

1602 (C=O); ^{1}H NMR ($CDCl_3$) 11.20 (1H, br s, OH), 7.34-7.22 (5H, m, arom H), 4.58 (2H, s, CH_2), 4.38 (2H, q, J = 7.21, CH_2), 3.84 (2H, s, H-5), 1.39 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 183.8, 167.1 (C=O), 157.6 (C-4), 136.6 (arom C), 128.8 (2C), 128.1 (2C), 127.8 (arom CH), 98.6 (C-3), 61.3, 49.0, 45.4 (CH_2), 14.2 (Me).

Methyl 1-Benzyl-4-hydroxy-3-pyrrolin-2-one-3-carboxylate (2b): pale-yellow microcrystals (from benzene-hexane), mp 116 °C ; IR (KBr) 3700-3250 (OH), 1708, 1591 (C=O); ^{1}H NMR (DMSO-d_6) 7.66-7.19 (5H, m, arom H), 5.5 (1H, br s, OH), 4.48 (2H, s, CH_2), 3.85 (2H, s, H-5), 3.66 (3H, s, Me); ^{13}C NMR (DMSO-d_6) 179.2, 167.5 (C=O), 162.3 (C-4), 137.9 (arom C), 128.6 (2C), 127.5 (2C), 127.2 (arom CH), 97.4 (C-3), 50.5 (Me), 49.3, 44.3 (CH_2). Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.49; H, 5.64; N, 5.87.

Ethyl 4-hydroxy-1-methyl-3-pyrrolin-2-one-3-carboxylate (2c): colorless microcrystals (from cold water), mp 189-191 °C (lit.,[17d] mp 190-192 °C); IR (KBr) 3700-3000 (OH), 1709, 1599 (C=O); ^{1}H NMR (DMSO-$d6$) 4.16 (2H, q, J = 7.21, CH_2), 3.80 (1H, br s, OH), 3.47 (2H, s, H-5), 2.83 (3H, s, Me), 1.26 (3H, t, J = 7.21, Me).

Ethyl 1-Ethyl-4-hydroxy-3-pyrrolin-2-one-3-carboxylate (2d): colorless needles (from chloroform-diethyl ether), mp 111-113 °C; IR (KBr) 3342 (OH), 1708, 1602 (C=O); ^{1}H NMR (DMSO-d_6) 5.60 (1H, br s, OH), 4.14 (2H, q, J = 6.84, CH_2), 3.96 (2H, s, H-5), 3.29 (2H, q, J = 7.33, CH_2), 1.21 (3H, t, J = 6.84, Me), 1.04 (3H, t, J = 7.33, Me); ^{13}C NMR (DMSO-d_6) 179.0, 167.0 (C=O), 162.3 (C-4), 98.0 (C-3), 59.0, 48.9, 35.4 (CH_2), 14.4, 13.3 (Me). Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.61; H, 6.42; N, 7.08.

Ethyl 1-Butyl-4-hydroxy-3-pyrrolin-2-one-3-carboxylate (2e): colorless microcrystals (from benzene-hexane), mp 97-100 °C; IR (KBr) 3600-3300 (OH), 1693, 1596 (C=O); ^{1}H NMR (DMSO-d_6) 5.60 (1H, br s, OH), 4.13 (2H, q, J = 7.33, CH_2), 3.94 (2H, s, H-5), 3.25 (2H, t, J = 7.33, CH_2), 1.42 (2H, m, CH_2), 1.22 (2H, m, CH_2), 1.20 (3H, t, J = 7.33, Me), 0.88 (3H, t , J = 7.33, Me); ^{13}C NMR (DMSO-d_6) 178.9, 167.3 (C=O), 162.3 (C-4), 97.8 (C-3), 59.0, 49.4, 40.2, 29.8, 19.5 (CH_2), 14.3, 13.6 (Me). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 58.11; H, 7.54; N, 6.21.

Ethyl 1-Isobutyl-4-hydroxy-3-pyrrolin-2-one-3-carboxylate (2f): colorless microcrystals (from benzene-hexane), mp 115 °C; IR (KBr) 3600-3200 (OH), 1708, 1600 (C=O); ^{1}H NMR (DMSO-d_6) 5.57 (1H, br s, OH), 4.13 (2H, q, J = 7.33, CH_2), 3.94 (2H, s, H-5), 3.06 (2H, d, J = 7.32, CH_2), 1.83 (1H, m, >CH-), 1.21 (3H, t, J = 7.33, Me), 0.82 (6H, d, J = 6.35, 2Me); ^{13}C NMR (DMSO-d_6) 178.9, 167.5 (C=O), 162.3 (C-4), 98.5 (C-3), 59.0, 50.0, 48.3 (CH_2), 27.0 (CH), 20.0 (2Me), 14.3 (Me). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.97; H, 7.14; N, 6.17.

Ethyl 4-Hydroxy-3-pyrrolin-2-one-3-carboxylate (2g): colorless microcrystals (from water), mp 141 °C (lit.,[16b] mp 140 °C); IR (KBr) 3600-3000 (NH, OH), 1721, 1658 (C=O); ^{1}H NMR (DMSO-d_6) 8.31 (1H, s, NH), 7.57 (1H, br s, OH), 4.13 (2H, q, J = 7.21, CH_2), 3.84 (2H, s, H-5), 1.21 (3H, t, J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 180.5, 170.5 (C=O), 162.6 (C-4), 98.0 (C-3), 58.8, 45.7 (CH_2), 14.2 (Me).

Methyl 4-Hydroxy-3-pyrrolin-2-one-3-carboxylate (2h): colorless microcrystals (from cold water), mp> 300 °C ; IR (KBr) 3600-3100 (NH, OH), 1690, 1612 (C=O); ^{1}H NMR (DMSO-d_6) 8.51 (1H, t, J = 5.71, NH), 7.50 (1H, br s, OH), 3.86 (2H, d, J = 5.71, H-5), 3.29 (3H, s, OMe); ^{13}C NMR (DMSO-d_6) 169.5 (C-4), 167.5, 165.7 (C=O), 78.0 (C-3), 60.4 (Me), 42.0 (CH_2). Anal. Calcd for $C_6H_7NO_4 \cdot 1/6H_2O$: C, 45.01; H, 4.41; N, 8.75. Found: C, 45.07; H, 4.62; N, 8.72.

1-Benzyl-3-cyano-4-hydroxy-3-pyrrolin-2-one (2i): pale-yellow microcrystals (from benzene-diethyl ether), mp 190-193 °C; IR (KBr) 3600-3100 (OH), 2226 (CN), 1600 (C=O); ^{1}H NMR (DMSO-d_6) 8.30 (1H, br s, OH), 7.39-7.10 (5H, m, arom H), 4.60 (2H, s, CH_2), 3.80 (2H, s, C-5); ^{13}C NMR (DMSO-d_6) 181.9 (C=O), 168.0 (C-4), 136.7 (arom C), 128.6 (2C), 127.6 (2C), 127.5 (arom CH), 113.2 (CN), 80.2 (C-3), 50.6, 45.3 (CH_2). Anal. Calcd for $C_{12}H_{10}N_2O_2 \cdot 1/6H_2O$: C, 66.35; H, 4.64; N, 12.90. Found: C, 66.54; H, 4.69; N, 13.30.

1-Butyl-3-cyano-4-hydroxy-3-pyrrolin-2-one (2j): colorless microcrystals (from benzene-hexane), mp 234-236 °C; IR (KBr) 3600-3200 (OH), 2224 (CN), 1606 (C=O); ^{1}H NMR (DMSO-d_6) 9.01 (1H, br s, OH), 4.03 (2H, s, H-5), 3.24 (2H, t, J = 7.21, CH_2), 1.44 (2H, quintet, J = 7.81, CH_2), 1.23 (2H, sextet,

J = 7.51, CH_2), 0.88 (3H, t , J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 182.1 (C=O), 166.8 (C-4), 113.3 (CN), 79.6 (C-3), 50.5, 40.6, 29.6, 19.3 (CH_2), 13.5 (Me). Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.55. Found: C, 59.86; H, 6.83; N, 15.27.

1-Benzyl-2,4-pyrrolidinedione (2k): The crystalline diketone (**2k**) was converted to a keto-enol mixture for 5 months in the air. Colorless microcrystals (from $CHCl_3$), mp 86-89 °C (mixture) (keto form: lit.,[17b] mp 64-66 °C); IR (KBr) 1772, 1701, 1640, 1599 (C=O); ^{1}H NMR ($CDCl_3$) 7.40-7.20 (5H, m, arom H), 4.63 (2H, s, CH_2), 3.73 (2H, s, CH_2), 3.09 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) 203.3 (C=O), 168.7 (C=O), 135.1 (arom C), 129.0 (2C), 128.4 (2C), 128.1 (arom C), 56.7, 46.0, 41.6 (CH_2).

Reaction of Alkenes (1a-n) with Pyrrolidinediones (2a-k) in the Presence of Manganese(III) Acetate in Acetic Acid at 23 °C under a Dry Air Stream. An alkene (**1**) (1 mmol), pyrrolidinedione (**2**) (2 mmol), manganese(III) acetate dihydrate (1 mmol), and glacial acetic acid (30 mL) were placed in a 50 mL three-necked flask equipped with a magnetic stirrer and gas inlet tube. The mixture was stirred at 23 °C under a dry air stream for the period of time shown in Table 1. The solvent was removed *in vacuo* and the residue was triturated with water followed by thrice extractions with chloroform (3 x 30 mL). The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated to dryness. The products were separated by TLC (Wakogel B 10) while eluting with 2% methanol-chloroform. The yields are listed in Table 1. The products were further purified for analytical samples by recrystallization from the appropriate solvent. Specific details are given below.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3aa): colorless microcrystals (from $CHCl_3$-EtOH), mp 211 °C; IR ($CHCl_3$) 3600-3150 (OH), 1744, 1703 (C=O); ^{1}H NMR ($CDCl_3$) 7.62-6.52 (15H, m, arom H), 5.14 (1H, s, OH), 4.65 (1H, d, J = 15.23, PhCHH_a), 4.18 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.07 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.87 (1H, d, J = 15.23, PhCHH_b), 3.55 (1H, d, J = 15.02, H_a-5), 3.48 (1H, d, J = 10.81, H_a-9), 3.29 (1H, d, J = 15.02, H_b-5), 2.93 (1H, d, J = 10.81, H_b-9), 1.16 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.4, 167.9 (C=O), 144.7, 140.2, 134.8 (arom C), 128.6 (2C), 128.3 (3C), 128.0 (2C), 127.6, 127.5 (2C), 127.4, 127.3 (2C), 125.2 (2C) (arom CH), 100.4 (C-1), 84.8 (C-4), 62.5, 53.6, 46.0, 30.8 (CH2), 56.7 (C-6), 13.8 (Me). Anal. Calcd for $C_{28}H_{27}NO_6$: C, 71.02; H, 5.75; N, 2.96. Found: C, 71.13; H, 5.75; N, 3.01.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-bis(4-methylphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]-nonan-7-one (3ba): colorless microcrystals (from $CHCl_3$-EtOH), mp 212 °C; IR (KBr) 3700-3100 (OH), 1734, 1673 (C=O); ^{1}H NMR ($CDCl_3$) 7.50-6.50 (13H, m, arom H), 4.98 (1H, s, OH), 4.74 (1H, d, J = 15.32, PhCHH_a), 4.20 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.08 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.84 (1H, d, J = 15.32, PhCHH_b), 3.50 (1H, d, J = 15.02, H_a-5), 3.48 (1H, d, J = 10.81, H_a-9), 3.27 (1H, d, J = 15.02, H_b-5), 2.93 (1H, d, J = 10.81, H_b-9), 2.31 (3H, s, Me), 2.23 (3H, s, Me), 1.18 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.4, 168.0 (C=O), 142.0, 137.4, 137.3, 136.7, 134.9 (arom C), 129.0 (2C), 128.7 (2C), 128.5 (2C), 127.4 (2C), 127.3, 127.2 (2C), 125.2 (2C) (arom CH), 100.3 (C-1), 84.8 (C-4), 62.5, 53.5, 45.9, 30.8 (CH_2), 56.8 (C-6), 21.1 (Me), 21.0 (Me), 13.9 (Me). Anal. Calcd for $C_{30}H_{31}NO_6$: C, 71.84; H, 6.23; N, 2.79. Found: C, 71.73; H, 6.18; N, 2.85.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-bis(4-methoxylphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]-nonan-7-one (3ca): colorless microcrystals (from $CHCl_3$-EtOH), mp 195 °C; IR (KBr) 3700-3100 (OH), 1726, 1677 (C=O); ^{1}H NMR ($CDCl_3$) 7.52-6.56 (13H, m, arom H), 4.82 (1H, br s, OH), 4.72 (1H, d, J = 15.32, PhCHH_a), 4.23 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.10 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.88 (1H, d, J = 15.32, PhCHH_b), 3.76 (3H, s, OMe), 3.70 (3H, s, OMe), 3.50 (1H, d, J = 10.81, H_a-9), 3.45 (1H, d, J = 15.02, H_a-5), 3.27 (1H, d, J = 15.02, H_b-5), 2.95 (1H, d, J = 10.81, H_b-9), 1.20 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.3, 168.1 (C=O), 158.9, 158.8, 137.1, 134.8, 132.3 (arom C), 128.7 (2C), 128.5 (2C), 127.5 (3C), 127.1 (2C), 113.6 (2C), 113.3 (2C) (arom CH), 100.3 (C-1), 84.7 (C-4), 62.5, 53.6, 46.0, 31.0 (CH_2), 56.8 (C-6), 55.2, 55.1 (OMe), 13.9 (Me). Anal. Calcd for $C_{30}H_{31}NO_8$: C, 67.53; H, 5.86; N, 2.63. Found: C, 67.50; H, 5.86; N, 2.60.

8-Benzyl-4,4-bis(4-chlorophenyl)-6-ethoxycarbonyl-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3da): colorless microcrystals (from $CHCl_3$-EtOH), mp 220 °C; IR (KBr) 3700-3000 (OH), 1733, 1669 (C=O); ^{1}H NMR (DMSO-d_6) 7.86 (1H, s, OH), 7.56-6.58 (13H, m, arom H), 4.66 (1H, d, J =

15.32, PhCHH_a), 4.25 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.13 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.58 (1H, d, J = 15.32, PhCHH_b), 3.50 (1H, d, J = 10.81, H_a-9), 3.35 (1H, d, J = 14.72, H_a-5), 3.16 (1H, d, J = 14.72, H_b-5), 2.92 (1H, d, J = 10.81, H_b-9), 1.23 (3H, t, J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 169.1, 167.3 (C=O), 143.3, 138.8, 134.9, 133.3, 132.9 (arom C), 128.9 (2C), 128.4 (2C), 128.3 (2C), 127.9 (2C), 127.3, 127.2 (2C), 126.9 (2C) (arom CH), 100.2 (C-1), 83.6 (C-4), 61.9, 54.1, 45.7, 30.4 (CH_2), 56.4 (C-6), 13.8 (Me). Anal. Calcd for $C_{28}H_{25}NO_6Cl_2$: C, 62.00; H, 4.65; N, 2.58. Found: C, 61.70; H, 4.59; N, 2.50.

8-Benzyl-6-ethoxycarbonyl-4,4-bis(4-fluorophenyl)-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ea): colorless needles (from $CHCl_3$-EtOH), mp 218 °C; IR (KBr) 3800-3000 (OH), 1740, 1682 (C=O); ^{1}H NMR (DMSO-d_6) 8.13 (1H, s, OH), 7.65-6.63 (13H, m, arom H), 4.57 (1H, d, J = 15.32, PhCHH_a), 4.21 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.09 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.99 (1H, d, J = 15.32, PhCHH_b), 3.53 (1H, d, J = 10.51, H_a-9), 3.48 (1H, d, J = 15.02, H_a-5), 3.06 (1H, d, J = 15.02, H_b-5), 2.93 (1H, d, J = 10.51, H_b-9), 1.16 (3H, t, J = 7.2, Me); ^{13}C NMR (DMSO-d_6) 168.8, 167.4 (C=O), 162.9, 159.7 (arom CF), 141.4, 136.6, 135.5 (arom C), 129.2, 129.1, 128.3 (2C), 127.3, 127.2, 127.1, 127.0 (2C), 115.3, 115.0, 114.7, 114.4 (arom CH), 100.1 (C-1), 83.2 (C-4), 61.7, 54.0, 44.9, 30.5 (CH_2), 56.2 (C-6), 13.7 (Me). Anal. Calcd for $C_{28}H_{25}NO_6F_2$: C, 66.00; H, 4.99; N, 2.73. Found: C, 66.19; H, 4.95; N, 2.76.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4-methyl-4-phenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3fa): colorless needles (from EtOH), mp 191 °C; IR (KBr) 3700-3000 (OH), 1744, 1672 (C=O); ^{1}H NMR ($CDCl_3$) 7.51-6.48 (10H, m, arom H), 5.17 (1H, br s, OH), 4.60 (1H, d, J = 15.32, PhCHH_a), 4.24 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.12 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.82 (1H, d, J = 15.32, PhCHH_b), 3.45 (1H, d, J = 10.81, H_a-9), 3.18 (1H, d, J = 14.72, H_a-5), 2.87 (1H, d, J = 14.72, H_b-5), 2.85 (1H, d, J = 10.81, H_b-9), 1.42 (3H, s, Me) 1.20 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.3, 168.0 (C=O), 141.9, 134.8 (arom C), 128.5 (2C), 127.9 (2C), 127.4 (2C), 127.3, 127.0, 126.0 (2C) (arom CH), 100.0 (C-1), 81.6 (C-4), 62.4, 53.6, 46.0, 30.0 (CH_2), 56.3 (C-6), 31.8, 13.9 (Me). Anal. Calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.04; H, 6.14; N, 3.58.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-dimethyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ga): colorless needles (from CH_2Cl_2-hexane), mp 153 °C; IR ($CHCl_3$) 3600-3100 (OH), 1740, 1701 (C=O); ^{1}H NMR ($CDCl_3$) 7.28 (5H, m, arom H), 5.06 (1H, s, OH), 4.75 (1H, d, J = 15.02, PhCHH_a), 4.33 (1H, d, J = 15.02, PhCHH_b), 4.16 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.05 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.57 (1H, d, J = 10.81, H_a-9), 3.14 (1H, d, J = 10.81, H_b-9), 2.50 (1H, d, J = 14.42, H_a-5), 2.33 (1H, d, J = 14.42, H_b-5), 1.26 (3H, s, Me), 1.22 (3H, s, Me), 1.11 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 170.4, 167.8 (C=O), 135.1 (arom C), 128.7 (2C), 128.3 (2C), 127.8 (arom CH), 100.2 (C-1), 77.6 (C-4), 62.3, 54.0, 46.9, 32.4 (CH_2), 56.4 (C-6), 27.9, 23.6, 13.8 (Me). Anal. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.90; H, 6.73; N, 4.02.

8-Benzyl-6-ethoxycarbonyl-4,4-diethyl-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ha): colorless needles (from CH_2Cl_2-hexane), mp 153 °C; IR (KBr) 3650-3150 (OH), 1750, 1700 (C=O); ^{1}H NMR ($CDCl_3$) 7.33-7.24 (5H, m, arom H), 5.26 (1H, s, OH), 4.68 (1H, d, J = 14.72, PhCHH_a), 4.40 (1H, d, J = 14.72, PhCHH_b), 4.17 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.15 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.56 (1H, d, J = 10.51, H_a-9), 3.14 (1H, d, J = 10.51, H_b-9), 2.44 (1H, d, J = 14.42, H_a-5), 2.26 (1H, d, J = 14.42, H_b-5), 1.76-1.31 (4H, m, 2 x CH_2), 1.12 (3H, t, J = 7.21, Me), 0.88 (3H, t, J = 7.51, Me), 0.82 (3H, t, J = 7.51, Me); ^{13}C NMR ($CDCl_3$) 170.7, 168.0 (C=O), 135.2 (arom C), 128.7 (2C), 128.3 (2C), 127.8 (arom CH), 100.2 (C-1), 81.8 (C-4), 62.3, 54.1, 46.8, 29.7, 28.6, 24.5 (CH_2), 56.1 (C-6), 13.8, 7.4, 6.9 (Me). Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.63; H, 7.22; N, 3.67.

14-Benzyl-12-ethoxycarbonyl-1-hydroxy-14-aza-2,3-dioxatricyclo[10.3.0.0^{4,11}]pentadecan-13-one (3ia): colorless needles (from $CHCl_3$-hexane), mp 182 °C; IR (KBr) 3700-3100 (OH), 1739, 1679 (C=O), ^{1}H NMR ($CDCl_3$) 7.34-7.14 (5H, m, arom H), 5.01 (1H, br s, OH), 4.55 (1H, d, J = 15.02, PhCHH_a), 4.42 (1H, d, J = 15.02, PhCHH_b), 4.35 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.24 (1H, dq, J = 10.81, 7.21, CHH_bMe), 4.21 (1H, m, H-4), 3.50 (1H, d, J = 10.81, H_a-15), 2.96 (1H, d, J = 10.81, H_b-15), 2.76 (1H, m, H-11), 1.77-1.38 (12H, m, 6 x CH_2), 1.32 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 170.0,

167.2 (C=O), 135.1 (arom C), 128.8 (2C), 127.9 (2C), 127.8 (arom CH), 101.8 (C-1), 81.4 (C-4), 62.6, 53.6, 46.9, 29.6, 26.1, 25.3, 24.7, 24.6, 22.3 (CH_2), 60.8 (C-12), 36.7 (C-11), 14.0 (Me). Anal. Calcd for $C_{22}H_{29}NO_6$: C, 65.49; H, 7.24; N, 3.47. Found: C, 65.46; H, 7.26; N, 3.53.

8-Benzyl-4-(4-chlorophenyl)-6-ethoxycarbonyl-1-hydroxy-4-phenyl-8-aza-2,3-dioxabicyclo[4.3.0]-nonan-7-one (3ja): colorless microcrystals (from $CHCl_3$-EtOH), mp 196 °C; IR (KBr) 3700-3000 (OH), 1743, 1681 (C=O); ^{1}H NMR ($CDCl_3$) 7.59-6.50 (14H, m, arom H), 5.58 (1H, br s, OH), 4.67 (1H, d, J = 15.02, PhCHH_a), 4.17 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.07 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.89 (1H, d, J = 15.02, PhCHH_b), 3.49 (1H, d, J = 10.81, H_a-9), 3.46 (1H, d, J = 15.02, H_a-5), 3.29 (1H, d, J = 15.02, H_b-5), 2.93 (1H, d, J = 10.81, H_b-9), 1.16 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.4, 167.7 (C=O), 143.7, 139.3, 134.6, 133.4, (arom C), 128.9, 128.6 (2C), 128.4 (2C), 128.2, 128.1, 127.9, 127.6, 127.4 (2C), 127.2, 126.7, 125.1 (arom CH), 100.4 (C-1), 84.5 (C-4), 62.6, 53.7, 46.0, 30.7 (CH_2), 56.7 (C-6), 13.8 (Me). Anal. Calcd for $C_{28}H_{26}NO_6Cl$: C, 66.21; H, 5.16; N, 2.76. Found: C, 66.07; H, 5.22; N, 2.85.

8-Benzyl-4-(4-bromophenyl)-6-ethoxycarbonyl-1-hydroxy-4-phenyl-8-aza-2,3-dioxabicyclo[4.3.0]-nonan-7-one (3ka): colorless microcrystals (from $CHCl_3$-EtOH), mp 215 °C; IR (KBr) 3700-3000 (OH), 1733, 1675 (C=O); ^{1}H NMR (DMSO-d_6) 8.09 (1H, s, OH), 7.60-6.59 (14H, m, arom H), 4.57 (1H, d, J = 15.32, PhCHH_a), 4.19 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.09 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.95 (1H, d, J = 15.32, PhCHH_b), 3.51 (1H, d, J = 14.12, H_a-5), 3.45 (1H, d, J = 10.81, H_a-9), 3.05 (1H, d, J = 14.12, H_b-5), 2.89 (1H, d, J = 10.81, H_b-9), 1.15 (3H, t, J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 168.7, 167.4 (C=O), 144.7, 140.2, 135.4, 120.6 (arom C), 131.2, 130.6, 129.2, 128.4 (2C), 128.3 (2C), 127.8, 127.1 (2C), 127.0 (2C), 126.8, 124.6 (arom CH), 100.1 (C-1), 83.3 (C-4), 61.6, 53.9, 44.9, 30.1 (CH_2), 56.2 (C-6), 13.7 (Me). Anal. Calcd for $C_{28}H_{26}NO_6Br$: C, 60.88; H, 4.74; N, 2.54. Found: C, 60.62; H, 4.76; N, 2.58.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4-(4-methoxyphenyl)-4-phenyl-8-aza-2,3-dioxabicyclo-[4.3.0]nonan-7-one (3la): colorless microcrystals (from EtOH), mp 95 °C; IR (KBr) 3700-3100 (OH), 1747, 1682 (C=O); ^{1}H NMR ($CDCl_3$) 7.53-6.58 (14H, m, arom H), 4.73 (1H, d, J = 15.32, PhCHH_a), 4.53 (1H, s, OH), 4.24 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.11 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.90 (1H, d, J = 15.32, PhCHH_b), 3.76 (3H, s, OMe), 3.51 (1H, d, J = 10.81, H_a-9), 3.50 (1H, d, J = 15.32, H_a-5), 3.25 (1H, d, J = 15.32, H_b-5), 2.98 (1H, d, J = 10.81, H_b-9), 1.21 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.6, 167.8 (C=O), 158.7, 145.0, 136.7, 134.7 (arom C), 128.6, 128.4 (3C), 128.2, 127.8, 127.3 (3C), 127.0 (2C), 125.2, 113.3 (2C) (arom CH), 100.2 (C-1), 84.6 (C-4), 62.3, 53.6, 45.9, 30.7 (CH_2), 56.7 (C-6), 55.0 (OMe), 13.7 (Me). Anal. Calcd for $C_{29}H_{29}NO_7$: C, 69.17; H, 5.80; N, 2.78. Found: C, 69.08; H, 6.00; N, 2.86.

8-Benzyl-4-(4-chlorophenyl)-6-ethoxycarbonyl-1-hydroxy-4-methyl-8-aza-2,3-dioxabicyclo[4.3.0]-nonan-7-one (3ma): colorless needles (from EtOH), mp 202 °C; IR (KBr) 3600-3000 (OH), 1745, 1670 (C=O); ^{1}H NMR ($CDCl_3$) 7.32-7.25 (9H, m, arom H), 4.91 (1H, s, OH), 4.77 (1H, d, J = 14.72, PhCHH_a), 4.37 (1H, d, J = 14.72, PhCHH_b), 4.08 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.03 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.61 (1H, d, J = 10.81, H_a-9), 3.27 (1H, d, J = 10.81, H_b-9), 2.83 (1H, d, J = 14.12, H_a-5), 2.69 (1H, d, J = 14.12, H_b-5), 1.50 (3H, s, Me), 1.10 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 170.2, 167.7 (C=O), 143.5, 135.0, 133.5 (arom C), 128.8 (2C), 128.5 (2C), 128.4 (2C), 128.0, 125.9 (2C) (arom CH), 101.0 (C-1), 80.3 (C-4), 62.5, 54.3, 46.9, 32.7 (CH_2), 56.9 (C-6), 25.3, 13.8 (Me). Anal. Calcd for $C_{23}H_{24}NO_6Cl$: C, 61.95; H, 5.43; N, 3.14. Found: C, 62.18; H, 5.54; N, 3.23.

8-Benzyl-4-(4-bromophenyl)-4-(4-chlorophenyl)-6-ethoxycarbonyl-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3na): colorless needles (from EtOH), mp 221 °C; IR (KBr) 3700-3100 (OH), 1733, 1674 (C=O); ^{1}H NMR (DMSO-d_6) 8.10 (1H, s, OH), 7.57-6.55 (13H, m, arom H), 4.57 (1H, d, J = 15.32, PhCHH_a), 4.20 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.07 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.92 (1H, d, J = 15.32, PhCHH_b), 3.48 (1H, d, J = 10.81, H_a-9), 3.44 (1H, d, J = 15.02, H_a-5), 2.95 (1H, d, J = 15.02, H_b-5), 2.84 (1H, dd, J = 10.81, H_b-9), 1.15 (3H, t, J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 168.6, 167.3 (C=O), 143.9, 139.4, 135.4, 132.3, 120.9 (arom C), 131.3, 130.7, 129.2, 128.9, 128.4, 128.3, 128.2, 127.8, 127.1, 127.0 (3C), 126.8 (arom CH), 100.1 (C-1), 83.1 (C-4), 61.7, 53.8,

44.9, 30.0 (CH_2), 56.1 (C-6), 13.7 (Me). Anal. Calcd for $C_{28}H_{25}NO_6BrCl$: C, 57.31; H, 4.29; N, 2.39. Found: C, 57.26; H, 4.34; N, 2.42.

8-Benzyl-1-hydroxy-6-methoxycarbonyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ab): colorless microcrystals (from $CHCl_3$-petroleum ether), mp 197 °C; IR (KBr) 3700-3100 (OH), 1754, 1678 (C=O); ^{1}H NMR ($CDCl_3$) 7.61-6.46 (15H, m, arom H), 5.53 (1H, br s, OH), 4.70 (1H, d, J = 15.32, PhCHH_a), 3.82 (1H, d, J = 15.32, PhCHH_b), 3.63 (3H, s, OMe), 3.55 (1H, d, J = 15.02, H_a-5), 3.47 (1H, d, J = 10.81, H_a-9), 3.29 (1H, d, J = 15.02, H_b-5), 2.91 (1H, d, J = 10.81, H_b-9); ^{13}C NMR ($CDCl_3$) 169.4, 168.5 (C=O), 144.7, 140.2, 134.7 (arom C), 128.6 (2C), 128.3 (2C), 128.0 (2C), 127.6, 127.4 (2C), 127.3, 127.2 (3C), 125.2 (2C) (arom CH), 100.3 (C-1), 84.7 (C-4), 56.7 (C-6), 53.5, 46.0, 30.8 (CH_2), 53.3 (OMe). Anal. Calcd for $C_{27}H_{25}NO_6$: C, 70.58; H, 5.48; N, 3.05. Found: C, 70.90; H, 5.46; N, 3.13.

6-Ethoxycarbonyl-1-hydroxy-8-methyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ac): colorless microcrystals (from EtOH), mp 199 °C; IR (KBr) 3700-3000 (OH), 1750, 1678 (C=O); ^{1}H NMR ($CDCl_3$) 7.54-7.17 (10H, m, arom H), 4.82 (1H, s, OH), 4.25 (1H, dq, J = 10.51, 7.21, CH_aHMe), 4.07 (1H, dq, J = 10.51, 7.21, CHH_bMe), 3.62 (1H, d, J = 10.81, H_a-9), 3.40 (1H, d, J = 14.72, H_a-5), 3.27 (1H, d, J = 14.72, H_b-5), 3.12 (1H, d, J = 10.81, H_b-9), 2.65 (3H, s, Me), 1.23 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 168.9, 168.3 (C=O), 144.5, 140.5 (arom C), 128.3 (2C), 127.8 (2C), 127.6, 127.2, 127.0 (2C), 125.1 (2C) (arom CH), 100.8 (C-1), 84.7 (C-4), 62.5, 56.4, 31.5 (CH_2), 56.1 (C-6), 29.5, 13.8 (Me). Anal. Calcd for $C_{22}H_{23}NO_6$: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.40; H, 6.11; N, 3.57.

6-Ethoxycarbonyl-8-ethyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ad): colorless needles (from EtOH), mp 185 °C; IR (KBr) 3700-3200 (OH), 1720, 1690 (C=O); ^{1}H NMR ($CDCl_3$) 7.57-7.16 (10H, m, arom H), 5.34 (1H, s, OH), 4.23 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.12 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.63 (1H, d, J = 10.51, H_a-9), 3.45 (1H, d, J = 15.02, H_a-5), 3.26 (1H, d, J = 15.02, H_b-5), 3.18 (1H, dq, J = 7.17, 7.06, NCHH_aMe), 3.09 (1H, d, J = 10.51, H_b-9), 2.97 (1H, dq, J = 7.21, 7.06, NCHH_bMe), 1.22 (3H, t, J = 7.21, Me), 0.70 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 168.5, 168.1 (C=O), 144.4, 140.2, (arom C), 128.2 (3C), 127.6 (3C), 127.1, 126.9, 125.2 (2C) (arom CH), 100.5 (C-1), 84.7 (C-4), 62.3, 53.8, 37.0, 31.0 (CH_2), 56.5 (C-6), 13.8, 11.3 (Me). Anal. Calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.43; H, 6.15; N, 3.47.

8-Butyl-6-Ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ae): colorless needles (from $CHCl_3$-EtOH), mp 185 °C; IR (KBr) 3600-3000 (OH), 1745, 1673 (C=O); ^{1}H NMR ($CDCl_3$) 7.58-7.15 (10H, m, arom H), 5.49 (1H, s, OH), 4.22 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.12 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.61 (1H, d, J = 10.51, H_a-9), 3.47 (1H, d, J = 15.02, H_a-5), 3.27 (1H, d, J = 15.02, H_b-5), 3.24 (1H, dt, J = 13.77, 6.70, NCHH_aPr), 3.10 (1H, d, J = 10.51, H_b-9), 2.86 (1H, dt, J = 13.77, 6.70, NCHH_bPr), 1.22 (3H, t, J = 7.21, Me), 1.13-0.83 (4H, m, 2 x CH_2), 0.73 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 169.0, 168.2 (C=O), 144.7, 140.2 (arom C), 128.3 (2C), 127.7 (2C), 127.6, 127.2 (2C), 127.0, 125.3 (2C) (arom CH), 100.6 (C-1), 84.8 (C-4), 62.4, 54.5, 42.1, 31.0, 28.6, 19.3 (CH_2), 56.7 (C-6), 13.9, 13.8 (Me). Anal. Calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.49; H, 6.60; N, 3.33.

6-Ethoxycarbonyl-1-hydroxy-8-isobutyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3af): colorless needles (from CH_2Cl_2-EtOH), mp 210 °C; IR (KBr) 3600-3000 (OH), 1724, 1679 (C=O); ^{1}H NMR ($CDCl_3$) 7.58-7.12 (10H, m, arom H), 5.34 (1H, s, OH), 4.23 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.13 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.62 (1H, d, J = 10.81, H_a-9), 3.48 (1H, d, J = 15.02, H_a-5), 3.27 (1H, d, J = 15.02, H_b-5), 3.12 (1H, d, J = 10.81, H_b-9), 3.06 (1H, dd, J = 13.52, 7.21, CH*H*a), 2.65 (1H, dd, J = 13.52, 7.21, CH*H*b), 1.56 (1H, m, -CH<), 1.22 (3H, t , J = 7.21, Me), 0.67 (3H, d, J = 6.61, Me), 0.40 (3H, d, J = 6.61, Me); ^{13}C NMR ($CDCl_3$) 169.3, 168.2 (C=O), 144.8, 140.2 (arom C), 128.3 (2C), 127.9 (2C), 127.6, 127.2, 127.1 (2C), 125.2 (2C) (arom CH), 100.6 (C-1), 84.8 (C-4), 62.4, 55.0, 50.0, 30.8 (CH_2), 56.7 (C-6), 26.3 (-CH<), 19.9, 19.2, 13.9 (Me). Anal. Calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.38; H, 6.41; N, 3.31.

6-Ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ag):

colorless needles (from CH_2Cl_2-EtOH), mp 212 °C; IR (KBr) 3600-3100 (NH and OH), 1729, 1713 (C=O); ^{1}H NMR (DMSO-d_6) 8.02 (1H, s, NH), 7.88 (1H, s, OH), 7.51-7.15 (10H, m, arom H), 4.19 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.08 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.43 (1H, d, J = 10.81, H_a-9), 3.31 (1H, d, J = 14.72, H_a-5), 2.98 (1H, d, J = 10.81, H_b-9), 2.95 (1H, d, J = 14.72, H_b-5), 1.17 (3H, t , J = 7.21, Me); ^{13}C NMR (DMSO-d_6) 170.7, 167.7 (C=O), 145.6, 141.0 (arom C), 128.2 (2C), 127.5 (2C), 127.3, 126.8 (2C), 126.7, 124.7 (2C) (arom CH), 100.2 (C-1), 83.4 (C-4), 61.4, 50.0, 29.8 (CH_2), 55.5 (C-6), 13.7 (Me). Anal. Calcd for $C_{21}H_{21}NO_6$: C, 65.79; H, 5.52; N, 3.65. Found: C, 65.55; H, 5.55; N, 3.78.

1-Hydroxy-6-methoxycarbonyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ah): colorless needles (from CH_2Cl_2-EtOH), mp 230 °C; IR (KBr) 3600-3000 (NH and OH), 1720, 1680 (C=O); ^{1}H NMR (DMSO-d_6) 8.05 (1H, s, NH), 7.93 (1H, s, OH), 7.53-7.15 (10H, m, arom H), 3.67 (3H, s, OMe), 3.44 (1H, d, J = 10.81, H_a-9), 3.36 (1H, d, J = 14.72, H_a-5), 2.98 (1H, d, J = 10.81, H_b-9), 2.96 (1H, d, J = 14.72, H_b-5); ^{13}C NMR (DMSO-d_6) 170.5, 168.3 (C=O), 145.6, 140.9, (arom C), 128.2 (2C), 127.5 (2C), 127.3, 126.7 (2C), 126.6, 124.7 (2C) (arom CH), 102.1 (C-1), 83.4 (C-4), 55.5 (C-6), 52.7 (Me), 49.8, 29.9 (CH_2). Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.18; N, 3.79. Found: C, 65.16; H, 5.17; N, 3.90.

8-Benzyl-6-cyano-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ai): colorless microcrystals (from CH_2Cl_2-EtOH), mp 207 °C; IR (KBr) 3500-2900 (OH), 2252 (CN), 1665 (CO); ^{1}H NMR (DMSO-d_6) 8.70 (1H, s, OH), 7.56-6.61 (15H, m, arom H), 4.54 (1H, d, J = 15.02, PhCHH_a), 4.06 (1H, d, J = 15.02, PhCHH_b), 3.68 (1H, d, J = 14.42, H_a-5), 3.54 (1H, d, J = 11.42, H_a-9), 3.06 (1H, d, J = 14.42, H_b-5), 3.03 (1H, d, J = 11.42, H_b-9); ^{13}C NMR (DMSO-d_6) 164.4 (C=O), 143.3, 140.8, 134.8 (arom C), 128.6 (2C), 128.3 (2C), 127.9 (2C), 127.8, 127.3, 127.2, 127.1 (2C), 126.4 (2C), 125.0 (2C) (arom CH), 116.7 (CN), 99.3 (C-1), 83.3 (C-4), 52.8, 45.3, 33.1 (CH_2), 46.4 (C-6) . Anal. Calcd for $C_{26}H_{22}N_2O_4$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.33; H, 5.20; N, 6.67.

8-Butyl-6-cyano-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3aj): colorless needles (from CH_2Cl_2-EtOH), mp 207 °C; IR (KBr) 3500-3000 (OH), 2253 (CN), 1674 (C=O); ^{1}H NMR (DMSO-d_6) 8.64 (1H, s, OH), 7.50-7.18 (10H, m, arom H), 3.54 (1H, d, J = 11.72, H_a-9), 3.47 (1H, d, J = 14.42, H_a-5), 3.32 (1H, d, J = 11.72, H_b-9), 3.19 (1H, dt, J = 13.82, 6.61, NCHH_aPr), 3.07 (1H, d, J = 14.42, H_b-5), 2.62 (1H, dt, J = 13.82, 6.61, NCHH_bPr), 1.09 (2H, m, CH_2), 0.83-0.67 (2H, m, CH_2), 0.70 (3H, t, J = 6.31, Me); ^{13}C NMR (DMSO-d_6) 164.1 (C=O), 143.1, 141.1, (arom C), 128.3 (2C), 127.7 (3C), 127.0, 126.2 (2C), 125.1 (2C) (arom CH),116.8 (CN), 99.7 (C-1), 83.3 (C-4), 53.3, 41.5, 33.6, 27.8, 18.6 (CH_2), 46.6 (C-6), 13.5 (Me). Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.34; H, 6.18; N, 7.22.

8-Benzyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ak): colorless microcrystals (from $CHCl_3$-EtOH), mp 190 °C; IR (KBr) 3600-3100 (OH), 1693 (C=O); ^{1}H NMR (DMSO-d_6) 7.66 (1H, s, OH), 7.59-6.56 (15H, m, arom H), 4.60 (1H, d, J = 15.62, PhCHH_a), 3.86 (1H, d, J = 15.62, PhCHH_b), 3.31 (1H, d, J = 11.11, H_a-9), 3.20 (1H, dd, J = 12.02, 3.00, H_a-5), 2.87 (1H, d, J = 11.11, H_b-9), 2.82 (1H, dd, J = 9.01, 3.00, H-6), 2.74 (1H, dd, J = 12.02, 9.01, H_b-5); ^{13}C NMR (DMSO-d_6) 170.8 (C=O), 144.6, 142.0, 135.8 (arom C), 128.3 (2C), 128.2 (2C), 127.7 (2C), 127.3, 126.9 (2C), 126.8 (2C), 126.7 (2C), 125.1 (2C) (arom CH), 99.9 (C-1), 83.7 (C-4), 54.1, 44.3, 28.5 (CH_2), 43.1 (CH). Anal. Calcd for $C_{25}H_{23}NO_4$: C, 74.79; H, 5.77; N, 3.49. Found: C, 75.01; H, 5.79; N, 3.67.

8-Benzyl-1-hydroxy-4,4-bis(4-methylphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3bk): colorless microcrystals (from $CHCl_3$-EtOH), mp 172 °C; IR (KBr) 3600-3100 (OH), 1691 (C=O); ^{1}H NMR ($CDCl_3$) 7.47-6.59 (13H, m, arom H), 4.96 (1H, s, OH), 4.75 (1H, d, J = 15.32, PhCHH_a), 3.78 (1H, d, J = 15.32, PhCHH_b), 3.29 (1H, d, J = 11.42, H_a-9), 3.14-3.06 (1H, m, H_a-5), 3.03 (1H, d, J = 11.42, H_b-9), 2.89-2.85 (2H, m, H_b-5 and H-6), 2.31 (3H, s, Me), 2.24 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 171.9 (C=O), 140.8, 138.9, 137.5, 136.7, 135.0 (arom C), 129.0 (2C), 128.7 (2C), 128.6 (2C), 127.4 (3C), 126.8 (2C), 125.6 (2C) (arom CH), 100.8 (C-1), 84.9 (C-4), 54.1, 44.3, 29.3 (CH_2), 45.6 (CH), 21.1, 21.0 (Me). Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.35; H, 6.60; N, 3.46.

8-Benzyl-1-hydroxy-4,4-bis(4-methoxylphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ck): colorless microcrystals (from $CHCl_3$-EtOH), mp 150 °C; IR (KBr) 3600-3100 (OH), 1690 (C=O); ^{1}H NMR ($CDCl_3$) 7.49-6.57 (13H, m, arom H), 5.78 (1H, s, OH), 4.76 (1H, d, J = 15.02, PhCHH_a), 3.73 (1H, d, J = 15.02, PhCHH_b), 3.72 (3H, s, OMe), 3.66 (3H, s, OMe), 3.29 (1H, d, J = 10.96, H_a-9), 3.11 (1H, br d, J = 12.02, H_a-5), 3.02 (1H, d, J = 10.96, H_b-9), 2.92-2.82 (2H, m, H_b-5 and H-6); ^{13}C NMR ($CDCl_3$) 172.1 (C=O), 158.9, 158.7, 136.3, 135.0, 133.7 (arom C), 128.6 (2C), 128.4 (2C), 127.4 (3C), 127.3 (2C), 113.5 (2C), 113.3 (2C) (arom CH), 100.5 (C-1), 84.7 (C-4), 55.1 (2OMe), 54.5, 45.6, 29.3 (CH_2), 44.2 (CH). Anal. Calcd for $C_{27}H_{27}NO_6$: C, 70.27; H, 5.90; N, 3.04. Found: C, 70.09; H, 5.95; N, 3.16.

8-Benzyl-4,4-bis(4-chlorophenyl)-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3dk): colorless microcrystals (from CH_2Cl_2-EtOH), mp 183 °C; IR (KBr) 3750-3000 (OH), 1670 (C=O); ^{1}H NMR (DMSO-d_6) 7.73 (1H, s, OH), 7.59-6.52 (13H, m, arom H), 4.65 (1H, d, J = 15.32, PhCHH_a), 3.79 (1H, d, J = 15.32, PhCHH_b), 3.32 (1H, d, J = 10.51, H_a-9), 3.24 (1H, dd, J = 12.02, 3.00, H_a-5), 2.82 (1H, dd, J = 9.01, 3.00, H-6), 2.81 (1H, d, J = 10.51, H_b-9), 2.65 (1H, dd, J = 12.02, 9.01, H_b-5); ^{13}C NMR (DMSO-d_6) 170.6 (C=O), 143.2, 140.1, 135.8, 132.3, 131.9 (arom C), 128.9 (2C), 128.3 (2C), 128.2 (2C), 127.7 (2C), 127.1 (2C), 126.9, 126.7 (2C) (arom CH), 99.7 (C-1), 83.1 (C-4), 53.9 44.3, 27.7 (CH_2), 42.7 (CH). Anal. Calcd for $C_{25}H_{21}NO_4Cl_2$: C, 63.84; H, 4.50; N, 2.98. Found: C, 63.85; H, 4.55; N, 3.09.

8-Benzyl-4,4-bis(4-fluorophenyl)-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ek): colorless microcrystals (from CH_2Cl_2-EtOH), mp 195 °C; IR (KBr) 3700-3000 (OH), 1672 (C=O); ^{1}H NMR (DMSO-d_6) 7.76 (1H, s, OH), 7.64-6.57 (13H, m, arom H), 4.66 (1H, d, J = 15.32, PhCHH_a), 3.84 (1H, d, J = 15.32, PhCHH_b), 3.35 (1H, d, J = 11.11, H_a-9), 3.24 (1H, dd, J = 12.02, 3.00, H_a-5), 2.87 (1H, d, J = 11.11, H_b-9), 2.84 (1H, dd, J = 9.01, 3.00, H-6), 2.72 (1H, dd, J = 12.02, 9.01, H_b-5); ^{13}C NMR (DMSO-d_6) 170.8 (C=O), 162.9, 159.7, 140.9, 137.5, 135.9 (arom C), 129.2, 129.1, 128.2 (2C), 127.6, 127.5, 127.0, 126.8 (2C), 115.2, 114.9, 114.6, 114.3 (arom CH), 99.8 (C-1), 83.2 (C-4), 54.1, 44.3, 28.2 (CH_2), 42.9 (CH). Anal. Calcd for $C_{25}H_{21}NO_4F_2$: C, 68.64; H, 4.84; N, 3.20. Found: C, 68.52; H, 4.83; N, 3.19.

8-Benzyl-1-hydroxy-4,4-dimethyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-7-one (3gk): colorless needles (from CH_2Cl_2-hexane), mp 120 °C; IR ($CHCl_3$) 3700-3100 (OH), 1687 (C=O); ^{1}H NMR ($CDCl_3$) 7.32-7.18 (5H, m, arom H), 5.11 (1H, br s, OH), 4.56 (1H, d, J = 14.72, PhCHH_a), 4.42 (1H, d, J = 14.72, PhCHH_b), 3.38 (1H, d, J = 11.11, H_a-9), 3.16 (1H, d, J = 11.11, H_b-9), 2.71 (1H, t, J = 7.51, H-6), 2.04 (2H, t, J = 7.51, H-5), 1.30 (3H, s, Me), 1.19 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 172.8 (C=O), 135.4 (arom C), 128.8 (2C), 128.0 (2C), 127.8 (arom CH), 100.5 (C-1), 77.9 (C-4), 54.4, 46.3, 30.3 (CH_2), 43.7 (CH), 26.8, 24.3 (Me). Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.88; H, 7.22; N, 5.03.

Manganese(III)-Based Reaction of 1,1-Diarylethenes (1a-e) with Pyrrolidinedione (2a) at 130 °C. 1,1-Diarylethene (**1**) (1 mmol) was placed in a 50 mL flask equipped with a magnetic stirrer. Glacial acetic acid (25 mL) and **2a** (522.2 mg, 2 mmol) were then added. The mixture was heated at reflux temperature and then manganese(III) acetate (804.1 mg, 3 mmol) was added. The mixture was stirred until the dark-brown color of Mn(III) disappeared. The reaction was quenched with water (50 mL) and the reaction mixture was extracted with chloroform (3 x 20 mL). The extract was washed with saturated sodium hydrogen carbonate solution (30 mL) and water (30 mL), dried over anhydrous sodium sulfate, filtered, and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10) with 1% MeOH-$CHCl_3$ as the developing solvent. The yields are listed in Table 2. The products were further purified by recrystallization to obtain analytical samples. Physical properties, which were obtained in pure state, are listed below.

3-(2-Acetoxy-2,2-diphenyl)ethyl-1-benzyl-3-ethoxycarbonyl-2,4-pyrrolidinedione (4a): colorless plates (from $CHCl_3$-hexane), mp 90 °C; IR ($CHCl_3$) 1783, 1750, 1696 (C=O); ^{1}H NMR ($CDCl_3$) 7.36-7.12 (15H, m, arom H), 4.82 (1H, d, J = 14.72, PhCHH_a), 4.15 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.13 (1H, d, J = 14.72, PhCHH_b), 4.08 (1H, dq, J = 10.81, 7.21, CH_bHMe), 3.87 (1H, d, J = 15.32, CH_aH), 3.77 (1H, d, J = 15.32, CH_bH), 3.48 (1H, d, J = 17.42, H_a-5), 2.92 (1H, d, J = 17.42, H_b-5), 2.12 (3H, s,

Ac), 1.23 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.5, 168.7, 167.8, 165.3 (C=O), 143.7, 143.5, 134.7 (arom C), 128.8 (2C), 128.4 (2C), 128.1 (3C), 128.0 (2C), 127.5, 127.4, 126.4 (2C), 125.8 (2C) (arom CH), 82.6 (>C<), 62.8, 55.0, 45.9, 36.4 (CH_2), 61.2 (C-3), 22.4, 13.7 (Me). Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.05; H, 5.90; N, 2.89.

3-[2-Acetoxy-2,2-bis(4-chlorophenyl)]ethyl-1-benzyl-3-ethoxycarbonyl-2,4-pyrrolidinedione (4d): colorless plates (from CH_2Cl_2-hexane), mp 222 °C; IR (KBr) 1781, 1750, 1699 (C=O); ^{1}H NMR ($CDCl_3$) 7.37-7.10 (13H, m, arom H), 4.78 (1H, d, J = 14.72, PhCHH_a), 4.16 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.06 (1H, dq, J = 10.81, 7.21, CH_bHMe), 4.00 (1H, d, J = 15.32, CHH_a), 3.92 (1H, d, J = 14.72, PhCHH_b), 3.74 (1H, d, J = 15.32, CHH_b), 3.59 (1H, d, J = 17.72, H_a-5), 3.06 (1H, d, J = 17.72, H_b-5), 2.12 (3H, s, Ac), 1.12 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.1, 168.5, 167.5, 165.0 (C=O), 141.8, 141.7, 134.5, 133.6, 133.5 (arom C), 128.8 (2C), 128.5 (2C), 128.3 (2C), 128.2 (3C), 127.7 (2C), 127.3 (2C) (arom CH), 81.8 (>C<), 63.0, 55.1, 46.0, 36.0 (CH_2), 61.0 (C-3), 22.3, 13.7 (Me). Anal. Calcd for $C_{30}H_{27}NO_6Cl_2$: C, 63.39; H, 4.79; N, 2.46. Found: C, 63.23; H, 4.84; N, 2.51.

3-[2-Acetoxy-2,2-bis(4-fluorophenyl)]ethyl-1-benzyl-3-ethoxycarbonyl-2,4-pyrrolidinedione (4e): colorless plates (from CH_2Cl_2-hexane), mp 170 °C; IR (KBr) 1781, 1750, 1699 (C=O); ^{1}H NMR ($CDCl_3$) 7.36-6.77 (13H, m, arom H), 4.78 (1H, d, J = 14.42, PhCHH_a), 4.18 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.07 (1H, dq, J = 10.81, 7.21, CH_bHMe), 4.06 (1H, d, J = 15.02, CHH_a), 3.99 (1H, d, J = 14.72, PhCHH_b), 3.71 (1H, d, J = 15.02, CHH_b), 3.56 (1H, d, J = 17.42, H_a-5), 3.01 (1H, d, J = 17.42, H_b-5), 2.11 (3H, s, Ac), 1.14 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.2, 168.6, 167.6, 165.1 (C=O), 163.4, 160.2, 139.5, 139.4, 134.6 (arom C), 128.9 (2C), 128.5 (2C), 128.3, 128.2 (2C), 127.9, 127.8, 115.2, 115.1, 114.9, 114.8 (arom CH), 81.9 (>C<), 62.9, 55.1, 46.0, 36.5 (CH_2), 61.1 (C-3), 22.4, 13.7 (Me). Anal. Calcd for $C_{30}H_{27}NO_6F_2$: C, 67.28; H, 5.08; N, 2.62. Found: C, 67.18; H, 5.09; N, 2.60.

1-Benzyl-3-ethoxycarbonyl-3-[2,2-bis(4-methylphenyl)ethenyl]-2,4-pyrrolidinedione (5b): colorless microcrystals (from CH_2Cl_2-hexane), mp 114 °C; IR (KBr) 1782, 1749, 1698 (C=O); ^{1}H NMR ($CDCl_3$) 7.30-6.95 (13H, m, arom H), 6.90 (1H, s, =CH-), 5.05 (1H, d, J = 14.72, PhCHH_a), 4.24 (1H, dq, J = 10.81, 7.21, CHH_aMe), 4.13 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.50 (1H, d, J = 17.41, H_a-5), 3.47 (1H, d, J = 14.72, PhCHH_b), 2.43 (1H, d, J = 17.41, H_b-5), 2.37 (3H, s, Me), 2.28 (3H, s, Me), 1.16 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.2, 168.4, 164.7 (C=O), 146.1, 137.6, 137.5, 137.4, 135.6, 134.5 (arom C and >C=), 130.1(2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 127.9 (2C), 127.7, 126.7 (2C) (arom CH), 121.0 (=CH-), 64.6 (C-3), 62.7, 55.1, 45.8 (CH_2), 21.0, 20.8, 13.5 (Me). Anal. Calcd for $C_{30}H_{29}NO_4$: C, 77.06; H, 6.25; N, 3.00. Found: C, 77.03; H, 6.27; N, 3.03.

1-Benzyl-3-ethoxycarbonyl-3-[2,2-bis(4-methoxyphenyl)ethenyl]-2,4-pyrrolidinedione (5c): colorless microcrystals (from CH_2Cl_2-hexane), mp 105 °C; IR (KBr) 1781, 1748, 1697 (C=O); ^{1}H NMR ($CDCl_3$) 7.32-6.76 (13H, m, arom H), 6.80 (1H, s, =CH-), 5.05 (1H, d, J = 14.72, PhCHH_a), 4.24 (1H, dq, J = 10.81, 7.21, CHH_aMe), 4.17 (1H, dq, J = 10.81, 7.21, CHH_bMe), 3.82 (3H, s, OMe), 3.76 (3H, s, OMe), 3.57 (1H, d, J = 14.72, PhCHH_b), 3.52 (1H, d, J = 17.42, H_a-5), 2.51 (1H, d, J = 17.42, H_b-5), 1.18 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.6, 168.8, 165.0 (C=O), 159.6, 159.2, 145.7, 134.9, 133.5, 131.3 (arom C and >C=), 131.8 (2C), 128.8 (2C), 128.3 (2C), 128.2 (2C), 128.0, 113.5 (2C), 113.4 (2C) (arom CH), 120.5 (=CH-), 65.0 (C-3), 63.0, 55.3, 46.1(CH_2), 55.4 (OMe), 55.2 (OMe), 13.8 (Me). Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.30; H, 5.90; N, 2.85.

Acid-Catalyzed Decomposition of 3aa and 3ca. A solution of **3aa** (1 mmol) in acetonitrile or acetic acid (15 mL) containing 60% perchloric acid (2 mL) was heated under reflux for one hour. The reaction was quenched with water (60 mL) and the reaction mixture was extracted with chloroform (3 x 20 mL). The extract was washed with saturated sodium hydrogen carbonate solution (30 mL) and water (30 mL), dried over anhydrous sodium sulfate, filtered, and concentrated to dryness. The residue was chromatographed on a silica gel plate while eluting with chloroform to give **6a** (33%). A similar reaction with **3ca** gave **6c** (55%).

1-Benzyl-3-ethoxycarbonyl-3-(2-phenyl-2-oxoethyl)-2,4-pyrrolidinedione (6a): liquid, IR ($CHCl_3$) 1783, 1743, 1697 (C=O); ^{1}H NMR ($CDCl_3$) 7.96-7.26 (10H, m, arom H), 5.06 (1H, d, J = 15.02, PhCHH_a), 4.48 (1H, d, J = 15.02, PhCHH_b), 4.27 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.25 (1H, d, J = 18.62, CHH_a), 4.19 (1H, dq, J = 10.81, 7.21, CH_bHMe), 4.12 (1H, d, J = 17.12, H_a-5), 4.05 (1H, d, J =

18.62, CHH_b), 3.99 (1H, d, J = 17.12, H_b-5), 1.24 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.1, 196.5, 168.7, 164.5 (C=O), 135.1, 135.0 (arom C), 134.1, 128.8 (2C), 128.7 (2C), 128.3 (2C), 128.1 (2C), 128.0 (arom CH), 63.0, 55.9, 46.5, 42.5 (CH_2), 60.5 (C-3), 13.9 (Me); MS *m/z* (rel intensity) 379 (M^+, 35), 306 (16), 242 (19), 214 (56), 105 (90), 91 (100), 77 (33). HRMS Found: *m/z* 379.1448. Calcd for $C_{22}H_{21}NO_5$: M, 379.1491.

1-Benzyl-3-ethoxycarbonyl-3-[2-(4-methoxyphenyl)-2-oxoethyl]-2,4-pyrrolidinedione (6c): colorless microcrystals (from CH_2Cl_2-hexane), mp 112 °C; IR ($CHCl_3$) 1782, 1742, 1697 (C=O); ^{1}H NMR ($CDCl_3$) 7.92 (2H, m, arom H), 7.40-7.30 (5H, m, arom H), 6.92 (2H, m, arom H), 5.07 (1H, d, J = 15.02, PhCHH_a), 4.45 (1H, d, J = 15.02, PhCHH_b), 4.25 (1H, dq, J = 10.81, 7.21, CH_aHMe), 4.21 (1H, d, J = 18.62, CHH_a), 4.17 (1H, dq, J = 10.81, 7.21, CH_bHMe), 4.12 (1H, d, J = 16.82, H_a-5), 4.01 (1H, d, J = 18.62, CHH_b), 3.97 (1H, d, J = 16.82, H_b-5), 3.87 (3H, s, OMe), 1.23 (3H, t, J = 7.21, Me); ^{13}C NMR ($CDCl_3$) 201.2, 194.8, 168.9, 164.7 (C=O), 164.2, 135.2, 128.1 (arom C), 130.8 (2C), 128.8 (2C), 128.1 (2C), 127.9, 113.9 (2C) (arom CH), 62.9, 55.9, 46.4, 42.3 (CH_2), 60.5 (C-3), 55.5, 13.8 (Me); MS *m/z* (rel intensity) 409 (M^+, 20), 336 (6), 272 (17), 214 (28), 135 (100), 107 (11), 91 (66), 77 (19). HRMS Found: *m/z* 409.1525. Calcd for $C_{23}H_{23}NO_6$: M, 409.1525.

X-Ray Crystallography of 3ga. A colorless prismatic crystal of $C_{18}H_{23}NO_6$ having the approximate dimensions of 0.80 x 0.60 x 0.60 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $47.59<2\theta<49.77°$ corresponded to a primitive orthorhombic cell with dimensions: a = 12.125(4), b = 26.971(4), c = 10.556(2) Å, V = 3452(1) Å^3, Z = 8, F.W. = 349.38, the calculated density is 1.34 g/cm^3, space group Pbca, F_{000} = 1488.00, μ(MoKα) = 1.01 cm^{-1}. A total of 3042 reflections was collected. The structure was solved by direct methods and expanded using Fourier techniques, R = 0.034, Rw = 0.019. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation. Details of the crystal structure determinations of **3ga** may be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB 21 E10, UK.

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