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Manganese(III)-based dioxapropellane synthesis using tricarbonyl compounds

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Abstract

The manganese(III)-induced oxidative cyclization of 3-(2-oxoethyl)piperidine-2,4-diones was conducted in the presence of 1,1-diarylethenes at reflux temperature to produce 3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-ones, simply called azadioxa[4.3.3]propellanes, in excellent yields. A similar oxidation of 2-(2-oxoethyl)cycloalkane-1,3-diones gave the corresponding [4.3.3]-, [5.3.3]-, and [6.3.3]-propellanes. The oxidation of 3-oxopropyl-substituted cycloalkane-1,3-diones also afforded the corresponding propellanes along with the 3-oxopropyl-substituted bicyclic intermediates. The bicyclic intermediates were definitely converted into the corresponding propellanes in the presence of a Lewis acid. The structure determination and the reaction pathway were also described.

1. Introduction

Propellanes containing a tricyclic system connected by a carbon–carbon single bond are one of the synthetic targets in organic synthesis due to their broad spectra of biological and pharmacological activities as well as their challenging molecular framework.[1] Some of these propellanes in nature display antibacterial,[2] antibiotic,[3] anticancer,[2b] antifungal,[4] and platelet-activating factor antagonistic activities.[5] Hence, many synthetic research groups have investigated the total synthesis of these natural products and their derivatives.[6] Some heterocycles containing the furopyridinone skeleton also possess antifungal and antibacterial effects.[7] For example, cladobotryal and its isomer derived from the metabolites of the fungus *Cladobotryum varium* have an inhibitory effect on the growth of plant pathogens and moderate activity against some drug-resistant bacteria.[7a]

In recent years, the manganese(III)-based oxidations have been developed by us and other research groups.[8] 1,3-Dicarbonyl compounds can readily form the manganese(III)-enolate complex in the presence of manganese(III) acetate in acetic acid. Subsequently, the enolate complex would provide the electron donor–acceptor-like complex with electron-rich alkenes followed by the one-electron oxidation to produce active carbon radicals.[9] These carbon radicals have then been used for the carbon–carbon bond formation, the peroxidation by trapping molecular oxygen,[10] and the generation of various important cyclic compounds in organic systhesis.[8a] Recently, we reported that the reaction of 1,1-disubstituted ethenes with 2-(2-oxoethyl)malonates in the presence of a stoichiometric amount of manganese(III) acetate in boiling acetic acid produced 2,8-dioxabicyclo[3.3.0]oct-3-enes via the cycloaddition–tandem cyclization.[11] The 2,8-dioxabicyclo[3.3.0]oct-3-ene skeleton is found in biologically and pharmacologically active compounds, such as the insect antifeedant, clerodin, isolated from *Clerodendrum infortunatum*.[12] Therefore, the manganese(III)-based tandem cyclization might be useful for the synthesis of functionalized 2,8-dioxabicyclo[3.3.0]oct-3-enes.

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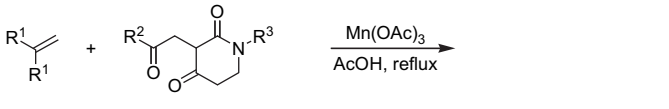
As a continuation of our study, we have advanced the manganese(III)-induced oxidation using 3-(2-oxoethyl)piperidine-2,4-diones in the hope of constructing novel and unique azadioxapropellanes, which possess both the furopyridinone and 2,8-dioxabicyclo[3.3.0]oct-3-ene frameworks.[13] In this paper, we report the successful synthesis of 3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-ones, the so-called azadioxa[4.3.3]propellanes, and their analogs derived from various oxoalkyl-substituted cyclic 1,3-dicarbonyl compounds using simple alkenes.

2. Results and discussion

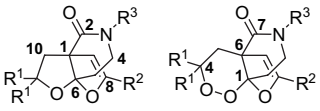
2.1. Manganese(III)-based oxidation of a mixture of various alkenes *1a–f* and 3-(2-oxoethyl)piperidine-2,4-diones *2a–i*

We initially attempted the oxidation of a mixture of 1,1-diphenylethene (**1a**) (0.5 mmol) and 1-benzyl-3-(2-oxo-2-phenylethyl)piperidine-2,4-dione (**2a**) (0.6 mmol) with manganese(III) acetate dihydrate (1.5 mmol) in glacial acetic acid (20 mL) at reflux temperature. The alkene **1a** was consumed within 1 min and four products were isolated after their chromatographic separation (Scheme 1 and Table 1, entry 1). The four products were determined by spectroscopic methods to be azadioxa[4.3.3]propellane **3aa** (53%) as the major product along with a small amount of by-products, azatrioxa[4.4.3]propellane **4aa** (9%), and an inseparable mixture of acetates **5aa** (13%) and **6aa** (13%) (vide infra).



1a-f **2a-i**

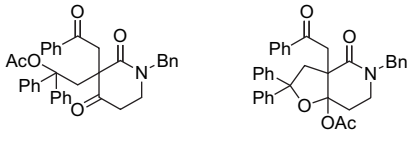
1a : R^1 = Ph
1b : R^1 = 4-Me-C_6H_4
1c : R^1 = 4-MeO-C_6H_4
1d : R^1 = 4-Cl-C_6H_4
1e : R^1 = 4-F-C_6H_4
1f : R^1 = 2-naphthyl



3 **4**

2a : R^2 = Ph, R^3 = Bn
2b : R^2 = 4-Me-C_6H_4, R^3 = Bn
2c : R^2 = 4-Cl-C_6H_4, R^3 = Bn
2d : R^2 = Ph, R^3 = Me
2e : R^2 = Ph, R^3 = Et
2f : R^2 = Ph, R^3 = Pr
2g : R^2 = Ph, R^3 = *i*-Pr
2h : R^2 = Ph, R^3 = Ph
2i : R^2 = *t*-Bu, R^3 = *t*-Bu

3aa, **4aa** : R^1 = Ph, R^2 = Ph, R^3 = Bn
3ba, **4ba** : R^1 = 4-Me-C_6H_4, R^2 = Ph, R^3 = Bn
3ca : R^1 = 4-MeO-C_6H_4, R^2 = Ph, R^3 = Bn
3da, **4da** : R^1 = 4-Cl-C_6H_4, R^2 = Ph, R^3 = Bn
3ea, **4ea** : R^1 = 4-F-C_6H_4, R^2 = Ph, R^3 = Bn
3ab, **4ab** : R^1 = Ph, R^2 = 4-Me-C_6H_4, R^3 = Bn
3ac, **4ac** : R^1 = Ph, R^2 = 4-Cl-C_6H_4, R^3 = Bn
3ad, **4ad** : R^1 = Ph, R^2 = Ph, R^3 = Me
3ae, **4ae** : R^1 = Ph, R^2 = Ph, R^3 = Et
3af, **4af** : R^1 = Ph, R^2 = Ph, R^3 = Pr
3ag, **4ag** : R^1 = Ph, R^2 = Ph, R^3 = *i*-Pr
3ah, **4ah** : R^1 = Ph, R^2 = Ph, R^3 = Ph
3fi : R^1 = 2-naphthyl, R^2 = *t*-Bu, R^3 = *t*-Bu



5 **6**

Scheme 1.

Table 1
Oxidation of a mixture of 1,1-diarylethenes **1** and 3-(2-oxoethyl)piperidine-2,4-diones **2** with manganese(III) acetate[a]

Entry	1	2	1/2/Mn(OAc)$_3$[b]	Time (min)	Product (yield,[c] %)	
1	**1a**	**2a**	1:1.2:3	1	**3aa** (53)	**4aa** (9)
2	**1b**	**2a**	1:1.3:3.5	1.5	**3ba** (90)	**4ba** (4)
3	**1c**	**2a**	1:1.3:3	1	**3ca** (94)	
4	**1a**	**2a**	1:1.2:3	10	**3aa** (87)	**4aa** (9)
5	**1d**	**2a**	1:1.6:4	10	**3da** (73)	**4da** (10)
6	**1e**	**2a**	1:1.5:3	10	**3ea** (62)	**4ea** (4)
7	**1a**	**2b**	1:1.5:3	10	**3ab** (80)	**4ab** (4)
8	**1a**	**2c**	1:1.5:3	10	**3ac** (93)	**4ac** (6)
9	**1a**	**2d**	1:1.5:3	10	**3ad** (87)	**4ad** (6)
10	**1a**	**2e**	1:1.5:3	10	**3ae** (78)	**4ae** (11)
11	**1a**	**2f**	1:1.5:3	10	**3af** (93)	**4af** (4)
12	**1a**	**2g**	1:1.5:3	10	**3ag** (86)	**4ag** (4)
13	**1a**	**2h**	1:1.5:3	10	**3ah** (90)	**4ah** (4)
14[d]	**1a**	**2a**	1:1.2:3	10	**3aa** (98)	
15[d]	**1a**	**2h**	1:1.5:3	10	**3ah** (93)	
16[d]	**1f**	**2i**	1:1.5:4	10	**3fi** (88)	

[a] The reaction of the alkene **1** (0.5 mmol) with 3-(2-oxoethyl)piperidine-diones **2** was carried out in glacial acetic acid (20 mL) in the presence of manganese(III) acetate dihydrate in air at reflux temperature.
[b] Molar ratio.
[c] Isolated yield based on the amount of the alkene **1** used.
[d] Before the oxidation, the mixture was degassed under reduced pressure for 30 min using an ultrasonicator followed by argon displacement, and freshly prepared manganese(III) acetate was used in the reaction.

A similar reaction of other alkenes **1b–e** with **2a–h** also gave similar results except for the reaction of **1c** with **2a** (Table 1, entry 3) (see Supplementary data). Since the azadioxapropellane **3aa** and the acetates **5** and **6** must be formed from the same intermediate, a mixture of acetates **5** and **6** was heated under reflux in acetic acid for 10 min. As a result, the acetates **5** and **6** were converted into the corresponding propellane **3aa** in a 92% isolated yield. Therefore, the continuous heating for 10 min after finishing the oxidation resulted in the exclusive production of the azadioxapropellanes **3** (Table 1, entries 4–13).

In our previous study, we reported the synthesis of azadioxabicyclo[4.4.0]decanones using the manganese(III)-catalyzed aerobic oxidation of 2,4-piperidinediones at ambient temperature.[8b] The endoperoxide ring was derived from the molecular oxygen dissolved in the solvent.[10] In fact, when the reaction was carried out using a sufficient amount of manganese(III) acetate at elevated temperature under argon, the azadioxabicyclodecanones were not produced, while only the azaoxabicyclo[4.3.0]nonanones were obtained.[8b] Therefore, in order to avoid the formation of the minor product **4**, the complete degassing under reduced pressure for 30 min using an ultrasonicator followed by argon displacement before the oxidation and also the use of freshly prepared manganese(III) acetate could control the formation of **4**, and the sole production of the azadioxapropellanes **3** was achieved (Table 1, entries 14–16).

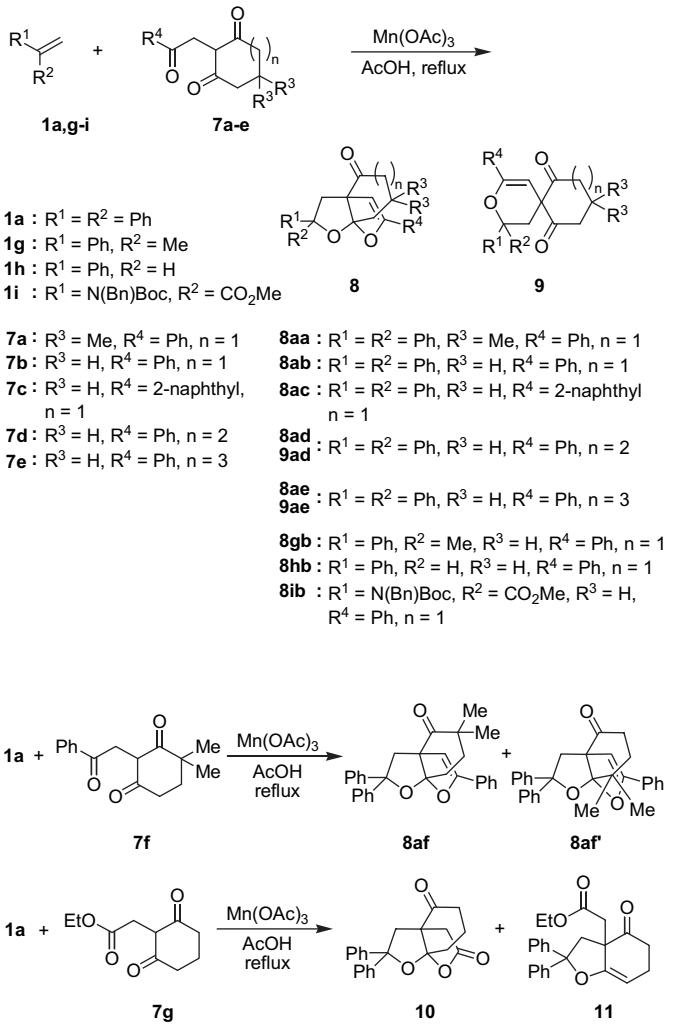
2.2. Structure determination

The ^{1}H NMR spectrum of **3aa** showed the two characteristic pairs of an AB quartet assigned to the benzyl protons and H-10 methylene protons at δ 4.66 (1H, d, J=14.9 Hz), 4.44

(1H, d, J=14.9 Hz), 3.59 (1H, d, J=13.4 Hz), and 2.97 (1H, d, J=13.4 Hz), respectively. One of the H-10 methylene protons (δ 2.97) might be shielded by the anisotropic effect of the alkenic double bond in the dihydrofuran ring. The most characteristic peak of the sp^2 proton (H-9) was confirmed at δ 5.19 (1H, s). The methylene protons of H-4 and H-5 appeared as a geminal and vicinal coupling pattern (ddd), respectively. In addition, one of the H-5 protons (δ 2.44) was shifted downfield compared to the corresponding methylene protons of 1-benzylpiperidine-2-one (calculated δ 1.55). It was supposed that the proton should locate the space adjacent to the dihydro- and tetrahydrofuran rings, in other words, it was suggested the three-dimensional structure having two fused furan rings. In the ^{13}C NMR spectrum, an amide carbonyl carbon appeared at δ 170.5, and two characteristic sp^2 carbons were observed at δ 156.3 (C-8) and δ 99.0 (C-9) due to a dihydrofuran ring. The peaks for the two quaternary carbons at the propellane axis appeared at δ 115.9 and 63.8 together with the quaternary carbon attached to the oxygen of tetrahydrofuran at δ 89.8. The chemical shift of these three quaternary carbons was quite similar to that of the azatrioxapropellane, of which the structure was characterized by X-ray crystallography.[8s] All the peaks in the NMR spectrum were also correlated by H–H COSY and H–C COSY. Furthermore, the absorption band at 1647 cm^{-1} was assigned to the amide carbonyl in the IR spectrum. Therefore, the structure was determined to be 3-benzyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo[4.3.3.$0^{1,6}$]dodec-8-en-2-one (**3aa**) based on these spectral data and the result of the high resolution FAB mass spectrum. The spectroscopic data of the minor product **4aa** were quite similar to those of the propellane **3aa** except for the ketal carbon at C-1, the quaternary carbon of the ring junction at C-6, and the quaternary carbon attached to the oxygen at C-4, which were slightly shifted upfield (4–9 ppm) in the ^{13}C NMR spectrum. The conclusive difference was the R_f value for the TLC and an extra oxygen in the FAB mass spectra as well as the combustion analysis (see Section 4). Accordingly, the minor product **4aa** was tentatively assigned as 8-aza-2,3,11-trioxa[4.4.3]propellane. The other minor products **5** and **6** were chromatographically inseparable, however, the acetate **5** could be isolated by fractional recrystallization from ethyl acetate–hexane.

2.3. Application of the propellane formation

In order to examine the applicability of the manganese(III)-based propellane formation, the reaction using 2-(2-oxoethyl)-cycloalkane-1,3-diones **7a–g** was carried out under similar oxidation conditions to give the desired propellanes **8** and **10** (Scheme 2 and Table 2). The ring size of the cycloalkanediones **7** was bigger, the yield of the propellanes **8** was lower, and the production of the spiroalkanes **9** was promoted (Table 2, entries 4 and 5). 2-Phenylpropene (**1g**) and styrene (**1h**) barely afforded **8gb** and **8hb**, respectively, together with an intractable mixture (Table 2, entries 6 and 7). The reaction using 2-methylpropene or 2-ethyl-1-butene became messy and no propellanes were isolated. 2-Aminoacrylate **1i** also gave **8ib** as a 1:1 diastereomixture (Table 2, entry 8). Although an excess amount of the oxidant was employed since **1i** was only converted in 60%, the yield of **8ib** did not increase (Table 2, entry 9). Dimethylcyclohexanedione **7f** produced isomeric propellanes **8af** and **8af'** (Table 2, entry 10). By using cyclohexanedioneacetate **7g**, the propellanelactone **10** was produced along with a bicyclic compound **11** (Table 2, entry 11).



Scheme 2.

A similar reaction using the 3-oxopropyl-substituted cycloalkanediones **12a–e** was next investigated. The cycloalkanediones **12a–c** gave the desired propellanes **13**, however, the bicyclic intermediates **14** were also isolated as a by-product (Scheme 3 and Table 3, entries 1–3). The continuous heating after finishing the oxidation did not effectively increase the yield of **13**. 2-(2-Oxocyclohexylmethyl)cyclohexane-1,3-dione (**12d**) gave a good result, though an excess amount of the oxidant was needed to consume **1a** (Table 3, entry 4). The reaction of cyclohexanedionepropanoate **12e** failed to produce the propellanelactone, but the bicyclic compounds **14ae** and **15** were obtained (Table 3, entry 5). In this case, the continuous heating resulted in decreased yields (Table 3, entry 6).

The quinoline and coumarin derivatives are found in a wide range of biologically active natural products.[14,15] Therefore, we next applied the propellane synthesis to the oxoalkyl-substituted

Table 2
Oxidation of a mixture of alkenes **1** and 2-(2-oxoethyl)cycloalkane-1,3-diones **7** with manganese(III) acetate[a]

Entry	1	7		Molar ratio[b]	Time (min)	Product (yield,[c] %)
1	**1a**	**7a**	n=1	1:1.5:3	10	**8aa** (80)
2	**1a**	**7b**	n=1	1:1.5:4	1	**8ab** (81)
3	**1a**	**7c**	n=1	1:1.5:4	5	**8ac** (80)
4	**1a**	**7d**	n=2	1:1.2:3	10	**8ad** (66)
						9ad (19)
5	**1a**[d]	**7e**	n=3	1:1.2:3	2	**8ae** (27)
						9ae (31)
6	**1g**	**7b**	n=1	1:1.5:4	5	**8gb** (17)[e]
7	**1h**	**7b**	n=1	1:2:2.5[f]	5	**8hb** (22)
8	**1i**[g]	**7b**	n=1	1:3:6	1	**8ib** (50)[e]
9	**1i**[h]	**7b**	n=1	1:3:10	1.5	**8ib** (44)[e]
10	**1a**	**7f**	n=1	1:1.7:4	5	**8af** (34)
						8af′ (32)
11	**1a**	**7g**	n=1	1:1.5:4	0.5	**10** (75)
						11 (19)

[a] The reaction of the alkene **1** (0.5 mmol) with 2-(2-oxoethyl)cycloalkanedione **7** was carried out in glacial acetic acid (20 mL) in the presence of manganese(III) acetate dihydrate at reflux temperature. Before the oxidation, the mixture was degassed under reduced pressure for 30 min using an ultrasonicator followed by argon displacement.
[b] Ratio of **1**/**7**/$Mn(OAc)_3$.
[c] Isolated yield based on the amount of the alkene **1** used.
[d] The alkene **1a** was recovered in 11%.
[e] The product was obtained as a 1:1 diastereomixture.
[f] Copper(II) acetate (0.75 mmol) was added as a co-oxidant.
[g] The alkene **1i** was recovered in 40%.
[h] The alkene **1i** was recovered in 24%.

4-hydroxyquinolinones **16a**,**b** and 4-hydroxycoumarin **16c** in order to functionalize their compounds. The reaction of **16a** gave an isomeric mixture of [4.3.3]propellanes **17aa** and **18** together with the intermediates **19** and **20aa** (Scheme 4 and Table 4, entry 1). The further heating for 30 min after finishing the oxidation of **16a** did not lead to an increased yield of the propellanes, but decreased the product yields. Quinolinone **16b** and coumarin **16c** gave the corresponding [4.4.3]propellanes **17ab** and **17ac** in excellent yields (Table 4, entries 2 and 4). The continuous heating after finishing the oxidation of **16b** was also not effective for the formation of **17ab** (Table 4, entry 3).

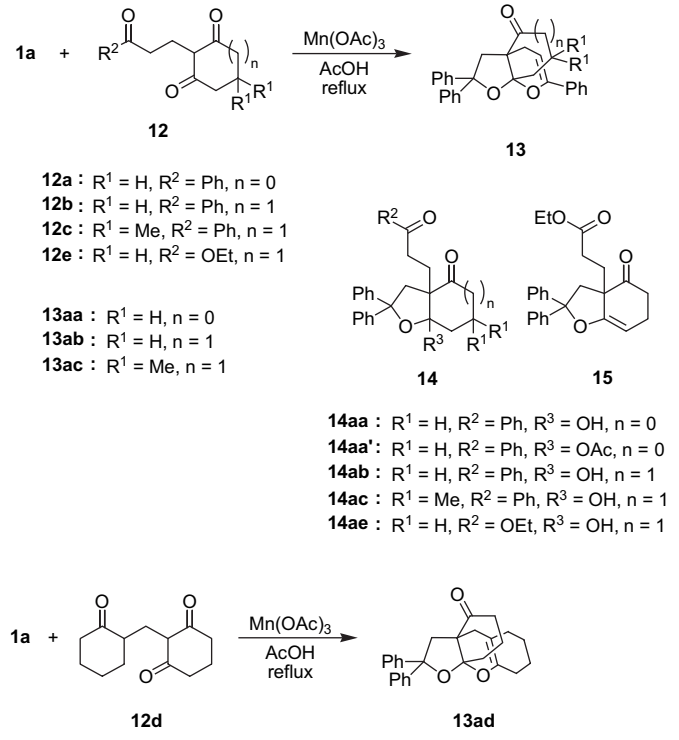
Table 3
Oxidation of a mixture of 1,1-diphenylethene (**1a**) and 2-(3-oxopropyl)-cycloalkane-1,3-diones **12a–e** with manganese(III) acetate[a]

Entry	Cycloalkane		Molar ratio[b]	Time (min)	Product (yield,[c] %)	
1	**12a**	n=0	1:1.2:3	10	**13aa** (21)	**14aa** (37)
						14aa′ (34)
2	**12b**	n=1	1:1.2:3	10	**13ab** (49)	**14ab** (31)
3	**12c**	n=1	1:1.5:3.5	10	**13ac** (47)	**14ac** (27)
4	**12d**	n=1	1:2:8	10	**13ad** (81)	
5[d]	**12e**	n=1	1:1.5:4	1	**14ae** (79)	**15** (10)
6[d]	**12e**	n=1	1:1.5:4	10	**14ae** (61)	**15** (19)

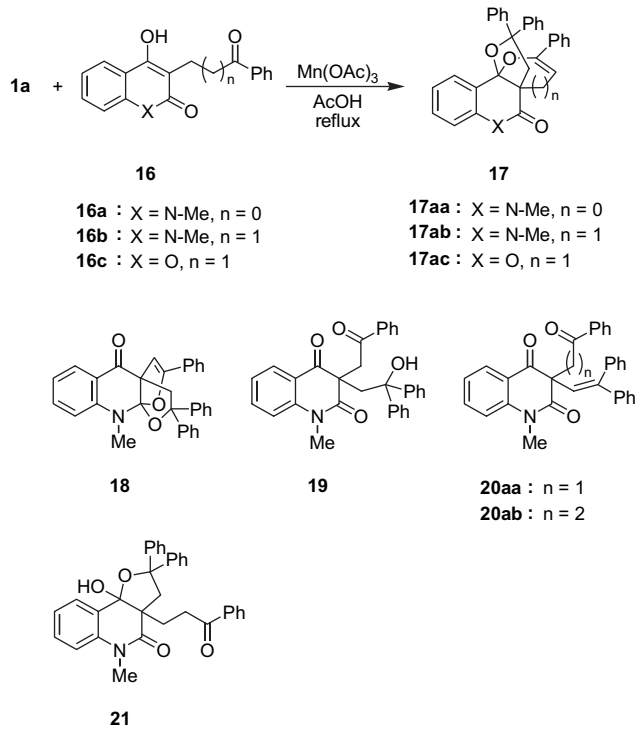
[a] The reaction of **1a** (0.5 mmol) with 2-(3-oxopropyl)cycloalkanedione **12** was carried out in glacial acetic acid (20 mL) in the presence of manganese(III) acetate dihydrate in air at reflux temperature.
[b] Ratio of **1a**/**12**/$Mn(OAc)_3$.
[c] Isolated yield based on the amount of **1a** used.
[d] Before the oxidation, the mixture was degassed under reduced pressure for 30 min using an ultrasonicator followed by argon displacement.

2.4. Lewis acid-induced cyclization of propellane intermediates

The propellane formation using the 3-oxopropyl-substituted cycloalkanediones **12** deserves comment. Since the continuous



Scheme 3.

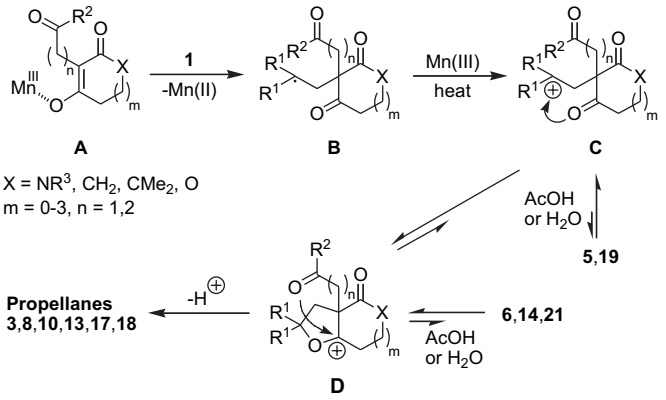


Scheme 4.

Table 4
Oxidation of a mixture of 1,1-diphenylethene (**1a**) and cyclic diketones **16a–c** with manganese(III) acetate[a]

Entry	Cycloalkane		Molar ratio[b]	Time (min)	Product (yield,[c] %)	
1	**16a**	n=0	1:1.2:3	10	**17aa** (32)	**18** (7)
					19 (33)	**20aa** (19)
2	**16b**	n=1	1:1.2:4	1	**17ab** (96)	
3	**16b**	n=1	1:1.2:4	10	**17ab** (43)	**20ab** (14)
						21 (16)
4	**16c**	n=1	1:1.5:4.5	0.5	**17ac** (84)	

[a] The reaction of **1a** (0.5 mmol) with **16** was carried out in glacial acetic acid (20 mL) in the presence of manganese(III) acetate dihydrate at reflux temperature. Before the reaction, the mixture was degassed under reduced pressure for 30 min using an ultrasonicator followed by argon displacement.
[b] Ratio of **1a/16**/$Mn(OAc)_3$.
[c] Isolated yield based on the amount of **1a** used.



Scheme 5.

heating after finishing the oxidation was not effective for the propellane formation and a considerable amount of the bicyclic propellane precursors **14** was obtained, the acid-catalyzed decomposition of the propellane **13ac** was examined. When the propellane **13ac** was treated with 2 M HCl in a 1:1 mixture of tetrahydrofuran and chloroform at reflux temperature, the ring-opened bicyclic hydroxide **14ac** was quantitatively obtained (93% yield). Therefore, the propellanes **13** might be sensitive to acidic media. We next investigated the forced transformation of the bicyclic hydroxides **14** into the corresponding propellanes **13**. The reaction was carried out in dry tetrahydrofuran using various Lewis acids, and the propellane formation was eventually achieved (Table 5). The use of ethyl aluminum dichloride or aluminum trichloride was effective for the cyclization (Table 5, entries 1, 3, 9, and 10).

2.5. Reaction pathway

The proposed mechanism for the formation of the dioxapropellanes is outlined in Scheme 5. The manganese(III)-based oxidative cycloaddition–tandem cyclization could be explained by a similar mechanism for the reaction using 2-(2-oxoethyl)malonates.[11,16] The enolate complex **A** would be formed by the reaction of the cyclic 1,3-diones with manganese(III) acetate during the first stage. It is known that the manganese(III)–enolate complex formation is the rate-determining step.[8a,9c] The enolate complex **A** easily oxidized the electron-rich alkenes **1** via a weak interaction between complex **A** and the alkene **1** such as an electron donor–acceptor-like complex,[9c] giving the corresponding tertiary carbon radicals **B**, which were rapidly oxidized by sufficient amounts of manganese(III) acetate under the stated conditions. As a result, the carbocations **C** would be formed and cyclize at the keto carbonyl oxygen of the cyclic 1,3-diones to produce the thermodynamically more stable carbocations **D**. The cations **D** would be allowed to intramolecularly cyclize at the carbonyl oxygen of the most appropriate position to finally produce the desired dioxapropellanes such as **3** and **8** by deprotonation. The by-products **5**, **6**, **14**, **19**, and **21** were formed by the attack of the acetate ion or water on cations **C** and **D**, however, the reaction should be reversible. Accordingly, the dioxapropellanes could be solely obtained when the dissolved molecular oxygen in the solvent was completely removed by degassing before the oxidation and the heating of the reaction mixture was continued for 10 min after the oxidation.

Table 5
Lewis acid-induced cyclization of propellane intermediates **14** and **21**[a]

Entry	Intermediate	Lewis acid	Conditions	Recovery (%)	Propellane (yield,[b] %)
1	**14aa**	$EtAlCl_2$ (4 equiv)	rt (30 min) then Reflux (30 min)		**13aa** (96)
2	**14ab**	$EtAlCl_2$ (4 equiv)	rt (30 min) then Reflux (30 min)		**13ab** (29)
3	**14ab**	$AlCl_3$ (4 equiv)	rt (5 h)	31	**13ab** (53)
4	**14ab**	$BF_3{\cdot}OEt_2$ (5 equiv)	Reflux (30 min)		**13ab** (9)
5	**14ab**	$FeCl_3$ (5 equiv)	Reflux (10 h)	55	**13ab** (24)
6	**14ab**	$CuCl_2$ (5 equiv)	Reflux (10 h)	52	**13ab** (29)
7	**14ab**	$TiCl_4$ (5 equiv)	rt (6 h) then 50–60 °C (1 h)	25	**13ab** (49)
8	**14ac**	$EtAlCl_2$ (4 equiv)	rt (30 min) then Reflux (30 min)		**13ac** (29)
9	**14ac**	$AlCl_3$ (4 equiv)	rt (5 h)	51	**13ac** (35)
10	**21**	$EtAlCl_2$ (4 equiv)	rt (30 min) then Reflux (1 h)		**17ab** (93)

[a] The reaction of the intermediate **14** or **21** (0.1 mmol) was carried out in dry tetrahydrofuran (2 mL) in air.
[b] Isolated yield based on the amount of the precursors **14** or **21** used.

3. Conclusion

We have accomplished the unique and selective synthesis of dioxapropellanes using the manganese(III)-based oxidation of the oxoalkyl-substituted cycloalkane-1,3-diones in the presence of alkenes **1**. However, the propellane formation was limited to the use of the alkenes such as 1,1-diarylethenes. Furthermore, the ring size of the cycloalkanediones **7** was bigger, the yield of the propellanes **8** was lower, and the production of spiroalkanes **9** were promoted. In addition, the oxopropyl-substituted cycloalkanediones **12** resisted the propellane formation and the bicyclic propellane precursors **14** were also isolated. The precursors **14** could be eventually converted into the corresponding propellanes **13** by the Lewis acid-mediated intramolecular cyclization. To the best of our knowledge, the propellane synthesis using the manganese(III)-based oxidative cyclization has never been reported. This propellane formation may be adaptable to various oxoalkyl-substituted cycloalkanediones.

4. Experimental

4.1. General

The NMR spectra were recorded using a JNM EX300 FT NMR spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm). The IR spectra of the neat samples were measured by the ATR method using a Shimadzu 8400 FTIR spectrophotometer and MIRacle A, and expressed in cm^{-1}. The EIMS spectra were recorded by a Shimadzu QP-5050A gas chromatograph–mass spectrometer at the ionizing voltage of 70 eV. The high resolution mass spectra were measured at the Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan. The elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan. Manganese(II) acetate tetrahydrate 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.[8b–m,9] The alkenes **1** were synthesized according to the literature,[7c,8e–m] except for **1g** and **1h**, which were purchased from Tokyo Kasei Co., Ltd.

4.2. Preparation of 3-(2-oxoethyl)piperidine-2,4-diones and their analogs

The 3-(2-oxoethyl)piperidine-2,4-dione derivatives **2a–i** were prepared by the reaction of the corresponding piperidine-2,4-diones with 2-bromoethanones in the presence of potassium carbonate in ethanol (see Supplementary data). The piperidinediones were synthesized by the Michael addition of alkyl acrylates with primary amines followed by condensation with alkyl malonyl chlorides and subsequent Dieckmann condensation in the presence of sodium ethoxide, and then decarboxylation by using 10% aqueous sulfuric acid at reflux temperature.[8b,17] The 2-(2-oxoethyl)cycloalkane-1,3-diones **7a–g** and 3-(2-oxoethyl)-1*H*-quinolin-2-one **16a** were also synthesized by a similar condensation as described above from the corresponding cycloalkane-1,3-diones or 4-hydroxy-1-methyl-1*H*-quinolin-2-one.[18] The 2-(3-oxopropyl)cycloalkane-1,3-diones **12a–c**, 3-(3-oxopropyl)-1*H*-quinolin-2-one **16b**, and 3-(3-oxopropyl)coumarin **16c** were produced by the reaction of the corresponding cyclic 1,3-diones with 1-aryl-3-dimethylaminopropan-1-ones (Mannich base) during the elimination of dimethylamine.[19]

4.3. Manganese(III)-based oxidation of a mixture of alkenes *1a–f* and triketones *2*, *7*, *12*, *16* at reflux temperature

The general procedure for the oxidation is as follows. An alkene **1** (0.5 mmol), triketone (0.6–1.5 mmol), and glacial acetic acid (20 mL) were placed in a 50 mL flask. Before the oxidation, the mixture was degassed under reduced pressure for 30 min using an ultrasonicator and then filled with argon. Manganese(III) acetate dihydrate (1.5–5.0 mmol) was quickly added to the reaction mixture followed by heating under reflux for 10 min (normally the brown color of manganese(III) disappeared within 1 min). The exact molar ratio of the alkene, triketone, and oxidant is shown in Tables 1–4. The solvent was removed in vacuo and the residue was triturated with water followed by extraction with chloroform (10 mL×3). The combined extracts were dried over anhydrous magnesium sulfate and then concentrated to dryness. The products were separated by a silica gel TLC (Wakogel B-10) while eluting with chloroform. The products were further purified by recrystallization from the appropriate solvents.

4.3.1. 3-Benzyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (*3aa*)

R_f=0.22 (chloroform); colorless oil; IR (neat) ν 1647 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.50 (2H, m, arom. H), 7.49–7.41 (2H, m, arom. H), 7.39–7.12 (13H, m, arom. H), 7.02–6.97 (2H, m, arom. H), 6.86–6.81 (2H, m, arom. H), 5.19 (1H, s, H-9), 4.66 (1H, d, J=14.9 Hz, Ph–CH_2), 4.44 (1H, d, J=14.9 Hz, Ph–CH_2), 3.59 (1H, d, J=13.4 Hz, H-10), 3.28 (1H, ddd, J=12.9, 10.5, 2.9 Hz, H-4), 3.13 (1H, ddd, J=12.9, 4.8, 3.9 Hz, H-4), 2.97 (1H, d, J=13.4 Hz, H-10), 2.49 (1H, ddd, J=13.6, 4.8, 2.9 Hz, H-5), 2.14 (1H, ddd, J=13.6, 10.5, 3.9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (C=O), 156.3 (C-8), 146.1, 144.4, 136.5, 129.2 (4C, arom. C), 128.7, 128.6, 128.2, 127.74, 127.65, 127.5, 127.4, 126.8, 126.3, 125.4, 125.23, 125.16 (20C, arom. *C*H), 115.9 (C-6), 99.0, 98.9 (1C, C-9), 89.8 (C-11), 63.8 (C-1), 50.1 (Ph–*C*H$_2$), 47.5 (C-10), 42.7 (C-4), 33.7 (C-5). FAB HRMS (acetone–NBA) calcd for $C_{34}H_{30}NO_3$ 500.2226 (M+1). Found 500.2229.

4.3.2. 3-Benzyl-11,11-bis(4-methylphenyl)-8-phenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (*3ba*)

R_f=0.38 (chloroform); colorless prisms; mp 167.0 °C; IR (neat) ν 1647 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.35 (2H, m, arom. H), 7.29–7.12 (12H, m, arom. H), 7.07–7.04 (2H, m, arom. H), 6.80–6.77 (2H, m, arom. H), 5.19 (1H, s, H-9), 4.66 (1H, d, J=14.7 Hz, Ph–CH_2), 4.41

(1H, d, J=14.7 Hz, Ph−CH_2), 3.53 (1H, d, J=13.4 Hz, H-10), 3.27 (1H, ddd, J=12.3, 10.8, 2.6 Hz, H-4), 3.11 (1H, ddd, J=12.3, 5.5, 3.9 Hz, H-4), 2.95 (1H, d, J=13.4 Hz, H-10), 2.45 (1H, ddd, J=13.6, 5.5, 2.6 Hz, H-5), 2.25 (3H, s, CH_3), 2.12 (1H, ddd, J=13.6, 10.8, 3.9 Hz, H-5), 1.98 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 (C=O), 156.2 (C-8), 143.3, 141.6, 136.5, 136.3, 135.6, 129.3 (6C, arom. C), 128.7, 128.6, 128.5, 128.1, 127.6, 127.3, 125.3, 125.2, 125.1 (18C, arom. *C*H), 115.8 (C-6), 99.1 (C-9), 89.6 (C-11), 63.8 (C-1), 50.0 (Ph−*C*H_2), 47.5 (C-10), 42.6 (C-4), 33.7 (C-5), 20.8, 20.5 (2C, *C*H_3). Anal. Calcd for $C_{36}H_{33}NO_3$: C, 81.95; H, 6.30; N, 2.65. Found: C, 82.17; H, 6.18; N, 2.60.

*4.3.3. 3-Benzyl-11,11-bis(4-methoxyphenyl)-8-phenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ca**)*

R_f=0.33 (chloroform); colorless oil; IR (neat) ν 1649 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46−7.43 (2H, m, arom. H), 7.29−7.13 (12H, m, arom. H), 6.81−6.78 (2H, m, arom. H), 6.55−6.52 (2H, m, arom. H), 5.21 (1H, s, H-9), 4.67 (1H, d, J=14.7 Hz, Ph−CH_2), 4.45 (1H, d, J=14.7 Hz, Ph−CH_2), 3.73 (3H, s, OCH_3), 3.48 (3H, s, OCH_3), 3.45 (1H, d, J=13.4 Hz, H-10), 3.29 (1H, ddd, J=12.8, 10.4, 2.8 Hz, H-4), 3.14 (1H, ddd, J=12.8, 5.0, 4.0 Hz, H-4), 2.95 (1H, d, J=13.4 Hz, H-10), 2.47 (1H, ddd, J=13.6, 5.0, 2.8 Hz, H-5), 2.14 (1H, ddd, J=13.6, 10.4, 4.0 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6 (C=O), 158.3, 157.9, 156.2 (3C, arom. C, C-8), 138.4, 136.8, 136.5, 129.4 (4C, arom. C), 128.7, 128.6, 127.7, 127.6, 127.4, 126.8, 126.7, 125.3 (14C, arom. *C*H), 115.9 (C-6), 113.4, 112.9 (4C, arom. *C*H), 99.24, 99.17 (1C, C-9), 89.5 (C-11), 64.0 (C-1), 55.11, 55.08, 54.97, 54.95 (2C, O*C*H_3), 50.1 (Ph−*C*H_2), 47.9 (C-10), 42.7 (C-4), 33.7 (C-5). FAB HRMS (acetone−NBA) calcd for $C_{36}H_{34}NO_5$ 560.2437 (M+1). Found 560.2438.

*4.3.4. 3-Benzyl-11,11-bis(4-chlorophenyl)-8-phenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3da**)*

R_f=0.28 (chloroform); colorless oil; IR (neat) ν 1643 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.39 (2H, m, arom. H), 7.31−7.14 (14H, m, arom. H), 6.99−6.96 (2H, m, arom. H), 5.17 (1H, s, H-9), 4.68 (1H, d, J=14.9 Hz, Ph−CH_2), 4.46 (1H, d, J=14.9 Hz, Ph−CH_2), 3.51 (1H, d, J=13.6 Hz, H-10), 3.32 (1H, ddd, J=12.7, 11.0, 2.4 Hz, H-4), 3.16 (1H, ddd, J=12.7, 5.3, 4.0 Hz, H-4), 2.89 (1H, d, J=13.6 Hz, H-10), 2.51 (1H, ddd, J=13.6, 5.3, 2.4 Hz, H-5), 2.11 (1H, ddd, J=13.6, 11.0, 4.0 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 (C=O), 156.6 (C-8), 144.2, 142.7, 136.4, 133.0, 132.5, 129.1 (6C, arom. C), 128.7, 128.5, 128.0, 127.8, 127.7, 127.6, 126.8, 126.6, 125.1 (18C, arom. *C*H), 116.0 (C-6), 98.9, 98.8 (1C, C-9), 88.9 (C-11), 63.8 (C-1), 50.2 (Ph−*C*H_2), 47.5 (C-10), 42.7 (C-4), 33.7 (C-5). FAB HRMS (acetone−NBA) calcd for $C_{34}H_{28}Cl_2NO_3$ 568.1446 (M+1). Found 568.1432.

*4.3.5. 3-Benzyl-11,11-bis(4-fluorophenyl)-8-phenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ea**)*

R_f=0.42 (chloroform); colorless oil; IR (neat) ν 1649 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47−7.14 (14H, m, arom. H), 7.08−6.91 (2H, m, arom. H), 6.73−6.66 (2H, m, arom. H), 5.19 (1H, s, H-9), 4.67 (1H, d, J=14.9 Hz, Ph−CH_2), 4.47 (1H, d, J=14.9 Hz, Ph−CH_2), 3.52 (1H, d, J=13.6 Hz, H-10), 3.31 (1H, ddd, J=13.0, 10.6, 2.6 Hz, H-4), 3.16 (1H, ddd, J=13.0, 4.6, 3.7 Hz, H-4), 2.91 (1H, d, J=13.6 Hz, H-10), 2.50 (1H, ddd, J=13.6, 4.6, 2.6 Hz, H-5), 2.13 (1H, ddd, J=13.6, 10.6, 3.7 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (C=O), 163.3, 163.0, 160.0, 159.8 (2C, arom. C), 156.5 (C-8), 141.9, 141.8, 140.2, 140.1, 136.5 (3C, arom. C), 129.1 (arom. *C*H), 129.0 (arom. C), 128.7, 128.4, 128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 127.1, 127.0, 126.9, 125.1 (13C, arom. *C*H), 116.0 (C-6), 115.2, 114.9, 114.5, 114.3 (4C, arom. *C*H), 98.9, 98.8 (1C, C-9), 89.1 (C-11), 63.9 (C-1), 50.2 (Ph−*C*H_2), 47.8 (C-10), 42.7 (C-4), 33.7 (C-5). FAB HRMS (acetone−NBA) calcd for $C_{34}H_{28}F_2NO_3$ 536.2037 (M+1). Found 536.2036.

*4.3.6. 3-Benzyl-8-(4-methylphenyl)-11,11-diphenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ab**)*

R_f=0.44 (chloroform); colorless microcrystals (from ethyl acetate−hexane); mp 128−129 °C; IR (KBr) ν 1636 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.49 (2H, m, arom. H), 7.41−7.38 (2H, m, arom. H), 7.35−7.11 (12H, m, arom. H), 7.03−6.98 (2H, m, arom. H), 6.88−6.83 (1H, m, arom. H), 5.12 (1H, s, H-9), 4.65 (1H, d, J=14.9 Hz, Ph−CH_2), 4.43 (1H, d, J=14.9 Hz, Ph−CH_2), 3.58 (1H, d, J=13.4 Hz, H-10), 3.28 (1H, ddd, J=12.7, 10.6, 2.4 Hz, H-4), 3.11 (1H, ddd, J=12.7, 5.0, 3.9 Hz, H-4), 2.97 (1H, d, J=13.4 Hz, H-10), 2.48 (1H, ddd, J=13.6, 5.0, 2.4 Hz, H-5), 2.28 (3H, s, CH_3), 2.12 (1H, ddd, J=13.6, 10.6, 3.9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 (C=O), 156.6 (C-8), 146.3, 144.6, 138.8, 136.6 (4C, arom. C), 128.7, 128.5, 128.2, 127.7, 127.6, 127.4, 126.9 (arom. *C*H), 126.6 (arom. C), 126.3, 125.4, 125.3 (arom. *C*H), 115.9 (C-6), 98.2 (C-9), 89.8 (C-11), 63.8 (C-1), 50.2 (Ph−*C*H_2), 47.6 (C-10), 42.8 (C-4), 33.7 (C-5), 21.3 (*C*H_3). Anal. Calcd for $C_{35}H_{31}NO_3$: C, 81.84; H, 6.08; N, 2.73. Found: C, 82.00; H, 6.26; N, 2.70. FAB HRMS (acetone−NBA) calcd for $C_{35}H_{32}NO_3$ 514.2382 (M+1). Found 514.2333.

*4.3.7. 3-Benzyl-8-(4-chlorophenyl)-11,11-diphenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ac**)*

R_f=0.53 (chloroform); colorless needles (from ethyl acetate−hexane); mp 174−175 °C; IR (KBr) ν 1645 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.48 (2H, m, arom. H), 7.39−7.37 (2H, m, arom. H), 7.27−7.14 (12H, m, arom. H), 7.02−6.97 (2H, m, arom. H), 6.87−6.82 (1H, m, arom. H), 5.18 (1H, s, H-9), 4.65 (1H, d, J=14.7 Hz, Ph−CH_2), 4.45 (1H, d, J=14.7 Hz, Ph−CH_2), 3.61 (1H, d, J=13.4 Hz, H-10), 3.26 (1H, ddd, J=13.0, 10.1, 2.9 Hz, H-4), 3.15 (1H, ddd, J=13.0, 5.1, 4.0 Hz, H-4), 2.91 (1H, d, J=13.4 Hz, H-10), 2.47 (1H, ddd, J=13.8, 5.1, 2.9 Hz, H-5), 2.16 (1H, ddd, J=13.8, 10.1, 4.0 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (C=O), 155.3 (C-8), 146.1, 144.3, 136.5, 134.5 (4C, arom. C), 128.7, 128.2, 128.03, 127.96, 127.8 (arom. *C*H), 127.7 (arom. C), 127.6, 127.5, 126.9, 126.6, 126.4, 125.4, 125.1 (arom. *C*H), 116.0 (C-6), 99.54, 99.51 (1C, C-9), 89.9 (C-11), 63.9 (C-1), 50.2 (Ph−*C*H_2), 47.5 (C-10), 42.7 (C-4), 33.7 (C-5). Anal.

Calcd for $C_{34}H_{28}ClNO_3$: C, 76.47; H, 5.28; N, 2.62. Found: C, 76.65; H, 5.32; N, 2.57. FAB HRMS (acetone–NBA) calcd for $C_{34}H_{29}ClNO_3$ 534.1836 (M+1). Found 534.1837.

4.3.8. 3-Methyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ad**)

R_f=0.20 (chloroform); colorless microcrystals (from ethyl acetate–hexane); mp 148.0 °C; IR (neat) ν 1636 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m, arom. H), 7.38–7.35 (2H, m, arom. H), 7.26–7.11 (8H, m, arom. H), 7.01–6.96 (2H, m, arom. H), 6.85–6.80 (1H, m, arom. H), 5.12 (1H, s, H-9), 3.55 (1H, d, J=13.4 Hz, H-10), 3.36 (1H, ddd, J=12.7, 10.5, 2.8 Hz, H-4), 3.14 (1H, ddd, J=12.7, 5.0, 4.0 Hz, H-4), 2.90 (3H, s, N–CH_3), 2.85 (1H, d, J=13.4 Hz, H-10), 2.55 (1H, ddd, J=13.4, 5.0, 2.8 Hz, H-5), 2.25 (1H, ddd, J=13.4, 10.6, 4.0 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 (C=O), 156.0 (C-8), 146.1, 144.3, 129.2 (3C, arom. C), 128.6, 128.0, 127.6, 127.4, 126.8, 126.2, 125.4, 125.3, 125.1 (15C, arom. *C*H), 115.8 (C-6), 99.1, 98.9 (1C, C-9), 89.8 (C-11), 63.4 (C-1), 47.5 (C-10), 45.4 (C-4), 34.9 (N–*C*H$_3$), 33.2 (C-5). Anal. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.39; H, 5.95; N, 3.26. FAB HRMS (acetone–NBA) calcd for $C_{28}H_{25}NO_3$ 423.1834 (M). Found 423.1830.

4.3.9. 3-Ethyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ae**)

R_f=0.20 (chloroform); colorless microcrystals (from chloroform–hexane); mp 137–138 °C; IR (neat) ν 1641 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.49 (2H, m, arom. H), 7.39–7.37 (2H, m, arom. H), 7.30–7.12 (8H, m, arom. H), 7.02–6.96 (2H, m, arom. H), 6.85–6.80 (1H, m, arom. H), 5.13 (1H, s, H-9), 3.55 (1H, d, J=13.4 Hz, H-10), 3.38 (2H, q, J=7.2 Hz, N–CH_2CH$_3$), 3.35–3.31 (1H, m, H-4), 3.18 (1H, ddd, J=12.8, 4.8, 3.9 Hz, H-4), 2.86 (1H, d, J=13.4 Hz, H-10), 2.56 (1H, ddd, J=13.6, 4.8, 2.8 Hz, H-5), 2.23 (1H, ddd, J=13.6, 10.5, 3.9 Hz, H-5), 1.04 (3H, t, J=7.2 Hz, N–CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8 (C=O), 156.0 (C-8), 146.2, 144.4, 129.3 (3C, arom. C), 128.6, 128.1, 127.7, 127.4, 126.8, 126.2, 125.4, 125.1 (15C, arom. *C*H), 115.8 (C-6), 99.1, 98.9 (1C, C-9), 89.8 (C-11), 63.6 (C-1), 47.5 (C-10), 42.8 (C-4), 42.0 (N–*C*H$_2$CH$_3$), 33.7 (C-5), 12.4, 12.2 (1C, N–CH$_2$*C*H$_3$). Anal. Calcd for $C_{29}H_{27}NO_3$: C, 79.61; H, 6.22; N, 3.20. Found: C, 79.46; H, 6.27; N, 3.11.

4.3.10. 3-Propyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**3af**)

R_f=0.22 (chloroform); colorless needles (from ethyl acetate–hexane); mp 137 °C; IR (neat) ν 163.8 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.49 (2H, m, arom. H), 7.40–7.37 (2H, m, arom. H), 7.26–7.14 (8H, m, arom. H), 7.01–6.97 (2H, m, arom. H), 6.85–6.82 (1H, m, arom. H), 5.13 (1H, s, H-9), 3.55 (1H, d, J=13.4 Hz, H-10), 3.42–3.15 (4H, m, N–CH_2CH$_2$CH$_3$, H-4), 2.84 (1H, d, J=13.4 Hz, H-10), 2.56 (1H, br d, J=13.6 Hz, H-5), 2.22 (1H, ddd, J=13.6, 10.5, 3.9 Hz, H-5), 1.49 (2H, sex, J=7.2 Hz, N–CH$_2$CH_2CH$_3$), 0.83 (3H, t, J=7.2 Hz, N–CH$_2$CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 (C=O), 156.1 (C-8), 146.2, 144.3, 129.3 (3C, arom. C), 128.6, 128.1, 127.7, 127.4, 126.7, 126.2, 125.4, 125.1 (15C, arom. *C*H), 115.8 (C-6), 99.1, 98.9 (1C, C-9), 89.7 (C-11), 63.7 (C-1), 48.7 (N–*C*H$_2$CH$_2$CH$_3$), 47.5 (C-10), 43.4 (C-4), 33.7 (C-5), 20.5 (N–CH$_2$*C*H$_2$CH$_3$), 11.1, 11.0 (1C, N–CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $C_{30}H_{29}NO_3$: C, 79.80; H, 6.47; N, 3.10. Found: C, 79.73; H, 6.47; N, 3.06. FAB HRMS (acetone–NBA) calcd for $C_{30}H_{30}NO_3$ 452.2226 (M+1). Found 452.2222.

4.3.11. 3-Isopropyl-8,11,11-triphenyl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ag**)

R_f=0.29 (chloroform); colorless needles (from chloroform–hexane); mp 137 °C; IR (neat) ν 1632 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (2H, m, arom. H), 7.41–7.38 (2H, m, arom. H), 7.25–7.11 (8H, m, arom. H), 7.01–6.95 (2H, m, arom. H), 6.84–6.79 (1H, m, arom. H), 5.14 (1H, s, H-9), 4.79 (1H, sep, J=6.8 Hz, N–C*H*(CH$_3$)$_2$), 3.55 (1H, d, J=13.4 Hz, H-10), 3.19–3.12 (2H, m, H-4), 2.87 (1H, d, J=13.4 Hz, H-10), 2.54 (1H, ddd, J=13.4, 4.8, 2.9 Hz, H-5), 2.14 (1H, ddd, J=13.4, 8.6, 5.5 Hz, H-5), 1.03 (3H, d, J=6.8 Hz, N–CH(CH_3)$_2$), 1.00 (3H, d, J=6.8 Hz, N–CH(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (C=O), 156.1 (C-8), 146.3, 144.5, 129.4 (3C, arom. C), 128.7, 128.2, 127.7, 127.5, 126.8, 126.2, 125.4, 125.2, 125.1 (15C, arom. *C*H), 115.7 (C-6), 99.0 (C-9), 89.8 (C-11), 63.9 (C-1), 47.7 (C-10), 44.0 (N–*C*H(CH$_3$)$_2$), 36.3 (C-4), 34.1 (C-5), 19.3, 19.2 (2C, N–CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{30}H_{29}NO_3$: C, 79.80; H, 6.47; N, 3.10. Found: C, 79.83; H, 6.71; N, 3.14. FAB HRMS (acetone–NBA) calcd for $C_{30}H_{29}NO_3$ 452.2226 (M+1). Found 452.2189.

4.3.12. 3,8,11,11-Tetraphenyl-3-aza-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**3ah**)

R_f=0.29 (chloroform); colorless microcrystals (from chloroform–hexane); mp 204.0 °C; IR (neat) ν 1655 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.52 (2H, m, arom. H), 7.44–7.42 (2H, m, arom. H), 7.39–7.17 (13H, m, arom. H), 7.16–6.99 (2H, m, arom. H), 6.87–6.82 (1H, m, arom. H), 5.21 (1H, s, H-9), 3.78 (1H, ddd, J=12.8, 10.5, 2.8 Hz, H-4), 3.64–3.60 (1H, m, H-4), 3.59 (1H, d, J=13.4 Hz, H-10), 3.03 (1H, d, J=13.4 Hz, H-10), 2.69 (1H, br d, J=13.6 Hz, H-5), 2.44 (1H, ddd, J=13.6, 10.5, 3.3 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0 (C=O), 156.5 (C-8), 146.1, 144.3, 142.5, 129.2 (4C, arom. C), 128.9, 128.8, 128.2, 127.8, 127.5, 126.9, 126.6, 126.3, 125.4, 125.25, 125.17 (20C, arom. *C*H), 115.8 (C-6), 98.9, 98.7 (1C, C-9), 90.0 (C-11), 64.3 (C-1), 47.7 (C-10), 46.9 (C-4), 34.2 (C-5). Anal. Calcd for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.67; H, 5.61; N, 2.87. FAB HRMS (acetone–NBA) calcd for $C_{33}H_{28}NO_3$ 486.2069 (M+1). Found 486.2098.

4.3.13. 3,8-Di-tert-butyl-11,11-dinaphthalen-2-yl-3-aza-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**3fi**)

R_f=0.23 (chloroform); colorless prisms (from diethyl ether–hexane); mp 234–235 °C; IR (KBr) ν 1649 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–7.38 (14H, m, arom. H), 4.62 (1H,

s, H-9), 3.70 (1H, d, J=13.7 Hz, H-10), 3.40 (1H, ddd, J=13.2, 4.9, 3.7 Hz, H-4), 3.22 (1H, ddd, J=13.2, 10.1, 2.0 Hz, H-4), 2.89 (1H, d, J=13.7 Hz, H-10), 2.43 (1H, ddd, J=13.4, 4.9, 2.0 Hz, H-5), 2.18 (1H, ddd, J=13.4, 10.1, 3.7 Hz, H-5), 1.37 (9H, s, N−C(CH_3)$_3$), 0.51 (9H, s, C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2 (C=O), 167.5 (C-8), 144.3, 141.9, 132.9, 132.6, 132.4, 132.1 (6C, arom. C), 128.2, 128.1, 128.0, 127.44, 127.39, 127.3, 126.0, 125.9, 125.8, 125.7, 125.5, 124.5, 124.0, 122.9 (14C, arom. *C*H), 115.7 (C-6), 96.3 (C-9), 89.7 (C-11), 65.4 (C-1), 57.5 (N−*C*(CH_3)$_3$), 46.5 (C-10), 39.6 (C-4), 35.0 (C-5), 31.5 (*C*(CH_3)$_3$), 28.4 (9C, N−C(*C*H_3)$_3$), 27.0 (9C, C(*C*H_3)$_3$). Anal. Calcd for $C_{37}H_{39}NO_3$: C, 81.43; H, 7.20; N, 2.57. Found: C, 81.15; H, 7.35; N, 2.52.

*4.3.14. 8-Benzyl-4,4,12-triphenyl-8-aza-2,3,11-trioxatricyclo[4.4.3.0^{1,6}]tridec-12-en-7-one (**4aa**)*

R_f=0.32 (chloroform); colorless microcrystals (from diethyl ether); mp 166.5 °C; IR (neat) ν 1639 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.54 (1H, m, arom. H), 7.43−7.12 (18H, m, arom. H), 5.13 (1H, s, H-13), 4.71 (1H, d, J=14.9 Hz, Ph−CH_2), 4.37 (1H, d, J=14.9 Hz, Ph−CH_2), 3.86 (1H, d, J=14.3 Hz, H-5), 3.38 (1H, ddd, J=12.7, 11.8, 2.8 Hz, H-9), 3.11 (1H, ddd, J=12.7, 4.6, 3.5 Hz, H-9), 2.69 (1H, d, J=14.3 Hz, H-5), 2.23 (1H, ddd, J=13.6, 3.5, 2.8 Hz, H-10), 1.95 (1H, ddd, J=13.6, 11.8, 4.6 Hz, H-10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3 (C=O), 156.3 (C-12), 146.8, 143.7, 136.3, 129.3 (4C, arom. C), 129.1, 128.7, 128.34, 128.27, 128.0, 127.7, 127.6, 127.1, 127.0, 125.42, 125.35, 125.2 (20C, arom. *C*H), 111.8 (C-1), 100.5, 100.4 (1C, C-13), 86.0 (C-4), 54.7 (C-6), 50.6 (Ph−*C*H_2), 41.4 (C-9), 37.1 (C-5), 27.9 (C-10). Positive FABMS (acetone−NBA) *m*/*z* 516 (M+1). Anal. Calcd for $C_{34}H_{29}NO_4$: C, 79.20; H, 5.67; N, 2.72. Found: C, 79.33; H, 5.60; N, 2.74.

*4.3.15. 1-Benzyl-3-(2-acetoxy-2,2-diphenylethyl)-3-(2-oxo-2-phenylethyl)piperidine-2,4-dione (**5**)*

R_f=0.20 (diethyl ether−hexane, 1:1, v/v); colorless microcrystals (from ethyl acetate−hexane); mp 182−183 °C; IR (neat) ν 1742, 1719, 1682, 1647 (C=O), 1221 (Ac); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60−7.24 (20H, m, arom. H), 4.98 (1H, d, J=14.9 Hz, Ph−CH_2), 3.90 (1H, d, J=14.9 Hz, Ph−CH_2), 3.62 (2H, s, CH_2), 3.52−3.34 (4H, m, H-6, CH_2), 2.82−2.67 (2H, m, H-5), 2.12 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6, 197.5, 171.3, 169.5 (4C, C=O), 145.1, 144.3, 136.5, 135.8 (4C, arom. C), 133.2, 128.6, 128.6, 128.4, 128.3, 128.1, 128.0, 127.5, 127.2, 127.1, 125.4 (20C, arom. *C*H), 83.9 (Ph$_2$>*C*), 56.2 (C-3), 50.8 (Ph−*C*H_2), 46.4 (*C*H_2), 41.4 (C-6, *C*H_2), 37.1 (C-5), 22.3 (Ac). Anal. Calcd for $C_{34}H_{29}NO_4$: C, 77.26; H, 5.94; N, 2.50. Found: C, 76.98; H, 5.95; N, 2.54.

*4.3.16. 4,4-Dimethyl-8,11,11-triphenyl-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**8aa**)*

R_f=0.66 (chloroform); colorless microcrystals (from chloroform−hexane); mp 165.0 °C; IR (neat) ν 1693 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.52 (2H, m, arom. H), 7.39−7.36 (2H, m, arom. H), 7.28−7.13 (8H, m, arom. H), 7.01−6.96 (2H, m, arom. H), 6.87−6.82 (1H, m, arom. H), 5.05 (1H, s, H-9), 3.46 (1H, d, J=13.2 Hz, H-10), 2.65 (1H, d, J=13.2 Hz, H-10), 2.56 (1H, d, J=14.5 Hz, H-5), 2.35 (1H, d, J=15.6 Hz, H-3), 2.26 (1H, d, J=15.6 Hz, H-3), 2.20 (1H, d, J=14.5 Hz, H-5), 1.05 (3H, s, CH_3), 0.95 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9 (C=O), 155.1 (C-8), 146.7, 144.8, 129.6 (3C, arom. C), 128.7, 128.2, 127.8, 127.6, 126.8, 126.2, 125.3, 125.0 (15C, arom. *C*H), 118.3 (C-6), 98.8, 98.6 (1C, C-9), 89.1 (C-11), 67.2 (C-1), 51.2 (C-3), 47.0 (C-5), 46.6 (C-10), 32.4 (C-4), 30.7, 30.6, 27.5, 27.3 (2C, *C*H_3). Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.29; H, 6.45.

*4.3.17. 8,11,11-Triphenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]-dodec-8-en-2-one (**8ab**)*

R_f=0.62 (chloroform); colorless microcrystals (from diethyl ether); mp 136 °C; IR (neat) ν 1703 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.48 (2H, m, arom. H), 7.38−7.35 (2H, m, arom. H), 7.28−7.16 (8H, m, arom. H), 7.03−6.98 (2H, m, arom. H), 6.87−6.82 (1H, m, arom. H), 4.89 (1H, s, H-9), 3.38 (1H, d, J=13.2 Hz, H-10), 2.75 (1H, d, J=13.2 Hz, H-10), 2.58−2.50 (2H, m, H-3, H-5), 2.36−2.25 (1H, m, H-5), 2.05−1.86 (3H, m, H-3, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4 (C=O), 157.4 (C-8), 146.4, 144.3, 129.4 (3C, arom. C), 128.9, 128.2, 127.8, 127.5, 126.9, 126.4, 125.7, 125.4, 125.2 (15C, arom. *C*H), 118.1 (C-6), 97.33, 97.28 (1C, C-9), 89.2 (C-11), 68.9 (C-1), 46.0 (C-10), 36.8 (C-5), 33.8 (C-3), 17.5 (C-4). Anal. Calcd for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.36; H, 5.97.

*4.3.18. 8-Naphthalen-2-yl-11,11-diphenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**8ac**)*

R_f=0.62 (chloroform); colorless needles (from chloroform−diethyl ether); mp 161 °C; IR (KBr) ν 1703 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79−6.70 (17H, m, arom. H), 5.02 (1H, s, H-9), 3.42 (1H, d, J=13.4 Hz, H-10), 2.77 (1H, d, J=13.4 Hz, H-10), 2.63−2.49 (2H, m, H-3, H-5), 2.37−2.26 (1H, m, H-5), 2.09−1.97 (1H, m, H-3), 1.90−1.87 (2H, m, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2 (C=O), 157.3 (C-8), 146.3, 144.2, 133.3, 132.7 (4C, arom. C), 128.4, 128.2, 127.5, 127.4, 126.9 (arom. *C*H), 126.6 (arom. C), 126.4, 126.3, 126.2, 125.6, 125.2, 124.6, 123.0 (arom. *C*H), 118.1 (C-6), 98.1 (C-9), 89.2 (C-11), 68.9 (C-1), 46.1 (C-10), 36.7 (C-5), 33.8 (C-3), 17.4 (C-4). Anal. Calcd for $C_{32}H_{26}O_3$: C, 83.82; H, 5.72. Found: C, 83.59; H, 5.51.

*4.3.19. 9,12,12-Triphenyl-8,13-dioxatricyclo[5.3.3.0^{1,7}]-tridec-9-en-2-one (**8ad**)*

R_f=0.78 (chloroform); colorless microcrystals (from diethyl ether); mp 143 °C; IR (KBr) ν 1703 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.77 (1H, m, arom. H), 7.55−7.09 (11H, m, arom. H), 6.99−6.94 (2H, m, arom. H), 6.84−6.79 (1H, m, arom. H), 4.83 (1H, s, H-10), 3.25 (1H, d, J=13.4 Hz, H-11), 3.05 (1H, d, J=13.4 Hz, H-11), 2.87 (1H, ddd, J=13.0, 11.2, 3.1 Hz, H-6), 2.75−2.69 (1H, m, H-6), 2.33−2.27 (1H, m, H-3), 1.79−1.66 (4H, m, H-4, H-5), 1.46−1.35 (1H, m, H-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5

(C=O), 157.2 (C-9), 146.9, 144.8, 137.5 (3C, arom. C), 130.0, 129.5, 128.8, 128.2, 128.0, 127.8, 127.5, 126.7, 126.0, 125.4, 125.3, 125.2 (15C, arom. *C*H), 117.3 (C-7), 99.9 (C-10), 89.2 (C-12), 73.0 (C-1), 43.9 (C-11), 40.0, 37.4, 26.8, 23.5 (4C, C-3, C-4, C-5, C-6). Anal. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20. Found: C, 82.44; H, 6.27. FAB HRMS (acetone–NBA) calcd for $C_{29}H_{27}O_3$ 423.1960 (M+1). Found 423.1958.

*4.3.20. 10,13,13-Triphenyl-9,14-dioxatricyclo[6.3.3.0^{1,8}]-tetradec-10-en-2-one (**8ae**)*

R_f=0.78 (chloroform); colorless oil; IR (KBr) ν 1697 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.44 (2H, m, arom. H), 7.35–7.32 (2H, m, arom. H), 7.26–7.12 (11H, m, arom. H), 7.00–6.95 (2H, m, arom. H), 6.85–6.80 (1H, m, arom. H), 4.96 (1H, s, H-11), 3.39 (1H, d, J=13.2 Hz, H-12), 3.04 (1H, d, J=13.2 Hz, H-12), 2.88 (1H, ddd, J=12.1, 6.4, 4.7 Hz, H-7), 2.57 (1H, ddd, J=15.8, 6.4, 2.6 Hz, H-3), 2.27 (1H, ddd, J=12.1, 10.6, 5.5 Hz, H-7), 1.97 (1H, ddd, J=15.8, 10.4, 3.3 Hz, H-3), 1.84–1.58 (5H, m, H-4, H-5, H-6), 1.27–1.20 (1H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1 (C=O), 157.1 (C-10), 147.0, 144.7, 129.7 (3C, arom. C), 128.8, 128.1, 127.8, 127.5, 126.7, 126.1, 125.7, 125.4, 125.3 (15C, arom. *C*H), 120.6 (C-8), 99.1 (C-11), 88.3 (C-13), 71.2 (C-1), 42.2, 35.8, 26.3, 24.7, 24.2 (5C, C-3, C-4, C-5, C-6, C-7). FAB HRMS (acetone–NBA) calcd for $C_{30}H_{29}O_3$ 437.2117 (M+1). Found 437.2119.

*4.3.21. 11-Methyl-8,11-diphenyl-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**8gb**) (stereoisomer **1**)*

R_f=0.56 (chloroform); colorless oil; IR (KBr) ν 1705 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70–7.19 (10H, m, arom. H), 5.39 (1H, s, H-9), 2.89 (1H, d, J=14.3 Hz, H-10), 2.67–2.23 (3H, m, CH_2), 2.08 (1H, d, J=14.3 Hz, H-10), 1.99–1.86 (3H, m, CH_2), 1.63 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.0 (C=O), 157.5 (C-8), 147.9, 129.6 (2C, arom. C), 129.4, 128.5, 128.2, 126.7, 125.6, 124.1 (10C, arom. *C*H), 119.2 (C-6), 98.8 (C-9), 86.3 (C-11), 69.1 (C-1), 47.2 (C-10), 36.7 (C-5), 34.0 (C-3), 30.3 (*C*H$_3$), 17.3 (C-4). FAB HRMS (acetone–NBA) calcd for $C_{23}H_{23}O_3$ 347.1647 (M+1). Found 347.1551.

*4.3.22. 11-Methyl-8,11-diphenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]-dodec-8-en-2-one (**8gb**) (stereoisomer **2**)*

R_f=0.39 (chloroform); colorless oil; IR (KBr) ν 1707 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–6.87 (10H, m, arom. H), 4.78 (1H, s, H-9), 2.94 (1H, d, J=13.2 Hz, H-10), 2.61–2.34 (3H, m, CH_2), 2.39 (1H, d, J=13.2 Hz, H-10), 1.99–1.86 (3H, m, CH_2), 1.56 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7 (C=O), 157.2 (C-8), 146.0, 129.5 (2C, arom. C), 128.8, 127.8, 127.5, 126.1, 125.3, 124.5 (10C, arom. *C*H), 118.1 (C-6), 97.1 (C-9), 86.6 (C-11), 69.0 (C-1), 46.4 (C-10), 36.7 (C-5), 34.0 (C-3), 32.6 (*C*H$_3$), 17.4 (C-4). FAB HRMS (acetone–NBA) calcd for $C_{23}H_{23}O_3$ 347.1647 (M+1). Found 347.1553.

*4.3.23. 8,11-Diphenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**8hb**)*

R_f=0.47 (chloroform); colorless oil; IR (KBr) ν 1705 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.64 (2H, m, arom. H), 7.50–7.26 (8H, m, arom. H), 5.28 (1H, s, H-9), 5.15 (1H, dd, J=11.4, 4.4 Hz, H-9), 2.66–2.37 (3H, m, CH_2), 2.54 (1H, dd, J=12.8, 4.4 Hz, H-10), 2.19 (1H, dd, J=12.8, 11.4 Hz, H-10), 2.11–1.94 (3H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5 (C=O), 159.0 (C-8), 139.0 (arom. C), 129.5 (2C, arom. *C*H), 129.3 (arom. C), 128.5, 128.0, 126.1, 125.6 (8C, arom. *C*H), 117.9 (C-6), 96.6 (C-9), 79.5 (C-11), 68.8 (C-1), 44.2 (C-10), 37.1 (C-5), 33.4 (C-3), 17.5 (C-4). FAB HRMS (acetone–NBA) calcd for $C_{22}H_{20}O_3$ 332.1412 (M). Found 332.1414.

*4.3.24. Methyl 8-(benzyl-tert-butoxycarbonylamino)-2-oxo-11-phenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-10-ene-8-carboxylate (**8ib**) (stereoisomer **1**)*

R_f=0.44 (diethyl ether–hexane, 1:1, v/v); colorless oil; IR (KBr) ν 1755, 1709 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.51 (2H, m, arom. H), 7.40–7.18 (8H, m, arom. H), 5.17 (1H, s, H-10), 4.87 (1H, d, J=16.5 Hz, Ph–CH_2), 4.55 (1H, d, J=16.5 Hz, Ph–CH_2), 3.51 (1H, s, CO_2CH_3), 3.44 (1H, d, J=14.3 Hz, H-9), 2.71 (1H, d, J=14.3 Hz, H-9), 2.45–2.39 (1H, m, CH_2), 2.19–2.15 (1H, m, CH_2), 2.06–1.94 (1H, m, CH_2), 1.74–1.58 (1H, m, CH_2), 1.42 (10H, s, C(CH_3)$_3$, CH_2), 1.04–0.96 (1H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9 (C=O), 169.7 (C=O), 157.5, 154.4 (2C, C=O, C-11), 140.1 (arom. C), 129.4 (arom. *C*H), 129.2 (arom. C), 128.4, 128.3, 126.6, 125.5 (9C, arom. *C*H), 119.0 (C-6), 98.4 (C-10), 95.3 (C-8), 81.8 (*C*(CH$_3$)$_3$), 67.6 (C-1), 52.8 (CO_2CH_3), 47.8 (C-9), 45.2 (Ph–*C*H$_2$), 36.6 (C-5), 32.7 (C-3), 28.2 (C(*C*H$_3$)$_3$), 17.0 (C-4). FAB HRMS (acetone–NBA) calcd for $C_{30}H_{33}NO_7$ 519.2257 (M). Found 519.2238.

*4.3.25. Methyl 8-(benzyl-tert-butoxycarbonylamino)-2-oxo-11-phenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]dodec-10-ene-8-carboxylate (**8ib**) (stereoisomer **2**)*

R_f=0.33 (diethyl ether–hexane, 1:1, v/v); colorless prisms (from diethyl ether–hexane); mp 140.0 °C; IR (KBr) ν 174.7, 1711 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.51 (2H, m, arom. H), 7.35–7.33 (3H, m, arom. H), 7.27–7.25 (2H, m, arom. H), 7.11–7.03 (3H, m, arom. H), 5.37 (1H, s, H-10), 4.47 (1H, d, J=16.2 Hz, Ph–CH_2), 4.44 (1H, d, J=16.2 Hz, Ph–CH_2), 3.66 (1H, s, CO_2CH_3), 3.60 (1H, d, J=14.7 Hz, H-9), 2.69 (1H, d, J=14.7 Hz, H-9), 2.52–2.36 (3H, m, CH_2), 2.07–2.00 (1H, m, CH_2), 1.88–1.77 (2H, m, CH_2), 1.36 (9H, s, C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6 (C=O), 170.4 (C=O), 156.0, 154.6 (2C, C=O, C-11), 139.1 (arom. C), 129.5 (arom. *C*H), 129.1 (arom. C), 128.4, 127.7, 126.4, 125.5 (9C, arom. *C*H), 120.7 (C-6), 99.7 (C-10), 95.0 (C-8), 81.4 (*C*(CH$_3$)$_3$), 66.9 (C-1), 52.7 (CO_2CH_3), 46.7 (2C, C-9, Ph–*C*H$_2$), 36.8 (C-5), 33.0 (C-3), 28.1 (C(*C*H$_3$)$_3$), 17.4 (C-4). Anal. Calcd for $C_{30}H_{33}NO_7$: C, 69.35; H, 6.40; N, 2.70. Found: C, 69.26; H, 6.46; N, 2.67.

*4.3.26. 3,3-Dimethyl-8,11,11-triphenyl-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**8af**)*

R_f=0.31 (chloroform–hexane, 5:5, v/v); colorless needles (from chloroform–diethyl ether); mp 199–200 °C; IR (KBr) ν 1697 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–6.83 (15H, m, arom. H), 4.88 (1H, s, H-9), 3.36 (1H, d, J=13.2 Hz, H-10), 2.77 (1H, d, J=13.2 Hz, H-10), 2.53 (1H, ddd, J=14.0, 5.9, 2.2 Hz, H-5), 2.04 (1H, ddd, J=14.0, 12.3, 2.6 Hz, H-5), 1.82 (1H, ddd, J=14.1, 12.3, 2.2 Hz, H-4), 1.66 (1H, ddd, J=14.1, 5.9, 2.6 Hz, H-4), 1.14 (3H, s, CH_3), 1.09 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.3 (C=O), 157.1 (C-8), 146.2, 144.4, 129.4 (3C, arom. C), 128.9, 128.2, 127.8, 127.5, 126.9, 126.3, 125.7, 125.4 (15C, arom. *C*H), 118.2 (C-6), 98.1 (C-9), 89.3 (C-11), 68.6 (C-1), 46.9 (C-10), 42.9 (C-3), 32.5 (C-5), 30.9 (C-4), 28.7, 26.6 (2C, *C*H$_3$×2). Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.46; H, 6.37.

*4.3.27. 5,5-Dimethyl-8,11,11-triphenyl-7,12-dioxatricyclo-[4.3.3.0^{1,6}]dodec-8-en-2-one (**8af′**)*

R_f=0.20 (chloroform–hexane, 5:5, v/v); colorless prisms (from diethyl ether–hexane); mp 173 °C; IR (KBr) ν 1701 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–6.76 (15H, m, arom. H), 4.74 (1H, s, H-9), 3.45 (1H, d, J=13.2 Hz, H-10), 2.64 (1H, d, J=13.2 Hz, H-10), 2.54 (1H, ddd, J=19.5, 8.6, 2.6 Hz, H-3), 2.38 (1H, ddd, J=19.5, 9.5, 8.6 Hz, H-3), 1.97 (1H, ddd, J=14.1, 9.5, 8.6 Hz, H-4), 1.58 (1H, ddd, J=14.1, 8.6, 2.6 Hz, H-4), 1.39 (3H, s, CH_3), 0.99 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2 (C=O), 157.7 (C-8), 146.8, 144.6, 129.4 (3C, arom. C), 128.9, 128.2, 127.7, 127.4, 126.6, 126.1, 125.4, 125.3, 124.9 (15C, arom. *C*H), 121.0 (C-6), 96.6 (C-9), 88.8 (C-11), 68.2 (C-1), 46.7 (C-10), 37.8 (C-5), 33.6 (C-3), 31.0 (C-4), 23.1, 22.2 (2C, *C*H$_3$×2). Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.80; H, 6.34.

*4.3.28. 9,11,11-Triphenyl-10-oxaspiro[6.5]dodec-9-ene-2,7-dione (**9ad**)*

R_f=0.53 (chloroform); colorless oil; IR (KBr) ν 1701 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.78 (2H, m, arom. H), 7.45–7.12 (13H, m, arom. H), 5.37 (1H, s, H-8), 3.35 (2H, s, H-12), 2.52–2.46 (2H, m, H-3, H-6), 2.38–2.32 (2H, m, H-3, H-6), 1.92–1.78 (4H, m, H-4, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8 (2C, C=O), 152.2 (C-9), 143.6, 134.5 (3C, arom. C), 129.0, 128.4, 128.3, 127.6, 125.9, 125.2 (15C, arom. *C*H), 93.9 (C-8), 81.2 (C-11), 65.1 (C-1), 40.1, 35.5, 28.6 (5C, C-3, C-4, C-5, C-6, C-12). FAB HRMS (acetone–NBA) calcd for $C_{29}H_{26}O_3$ 422.1882 (M). Found 422.1877.

*4.3.29. 10,12,12-Triphenyl-11-oxaspiro[7.5]tridec-10-ene-2,8-dione (**9ae**)*

R_f=0.67 (chloroform); colorless needles (from chloroform–hexane); mp 192–193 °C; IR (KBr) ν 1693 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.81 (2H, m, arom. H), 7.41–7.19 (13H, m, arom. H), 5.60 (1H, s, H-9), 3.34 (2H, s, H-13), 2.43–2.37 (4H, m, H-3, H-7), 1.68–1.47 (6H, m, H-4, H-5, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0 (2C, C=O), 152.1 (C-10), 143.6, 134.6 (3C, arom. C), 129.0, 128.4, 128.2, 127.5, 126.1, 125.2 (15C, arom. *C*H), 94.3 (C-9), 81.4 (C-12), 66.3 (C-1), 39.2 (C-13), 35.4, 26.3, 26.0 (5C, C-3, C-4, C-5, C-6, C-7). Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.48; H, 6.59.

*4.3.30. 11,11-Diphenyl-7,12-dioxatricyclo[4.3.3.0^{1,6}]-dodecane-2,8-dione (**10**)*

R_f=0.36 (chloroform–methanol, 98:2, v/v); colorless needles (from chloroform–diethyl ether); mp 164.0 °C; IR (KBr) ν 1786, 1715 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.18 (10H, m, arom. H), 3.29 (1H, d, J=13.6 Hz, H-10), 2.94 (1H, d, J=18.7 Hz, H-9), 2.88 (1H, d, J=13.6 Hz, H-10), 2.61–2.54 (1H, m, CH_2), 2.45–2.38 (2H, m, CH_2), 2.43 (1H, d, J=18.7 Hz, H-9), 1.99–1.89 (1H, m, CH_2), 1.85–1.68 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 171.7 (2C, C=O), 144.2, 144.0 (2C, arom. C), 128.5, 128.3, 127.6, 127.4, 125.4, 125.2 (10C, arom. *C*H), 117.3 (C-6), 90.7 (C-11), 60.9 (C-1), 46.6, 37.9, 36.2, 33.0, 17.0 (5C, *C*H$_2$). Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.91; H, 5.59.

*4.3.31. Ethyl 3-(4-oxo-2,2-diphenyl-2,3,5,6-tetrahydro-4H-benzofuran-3a-yl)acetate (**11**)*

R_f=0.49 (chloroform–methanol, 98:2, v/v); colorless oil; IR (KBr) ν 1734, 1719 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (2H, m, arom. H), 7.38–7.17 (8H, m, arom. H), 5.25 (1H, dd, J=9.2, 2.2 Hz, H-7), 4.02 (2H, q, J=7.0 Hz, O–CH_2CH$_3$), 3.25 (1H, d, J=13.6 Hz, H-3), 2.97 (1H, d, J=13.6 Hz, H-3), 2.73–2.59 (2H, m, CH_2), 2.58 (1H, d, J=14.3 Hz, CH_2–CO$_2$Et), 2.44–2.31 (2H, m, CH_2), 2.26 (1H, d, J=14.3 Hz, CH_2–CO$_2$Et), 1.18 (3H, t, J=7.0 Hz, O–CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.7, 169.5 (2C, C=O), 156.0 (C-7a), 145.9, 144.9 (2C, arom. C), 128.5, 128.3, 127.3, 127.2, 125.34, 125.32 (10C, arom. *C*H), 94.2 (C-7), 89.6 (C-2), 60.9 (O–*C*H$_2$CH$_3$), 55.5 (C-3a), 41.8, 39.0, 34.2, 20.0 (4C, *C*H$_2$), 14.0 (O–CH$_2$*C*H$_3$). FAB HRMS (acetone–NBA) calcd for $C_{24}H_{25}O_4$ 377.1753 (M+1). Found 377.1753.

*4.3.32. 3,8,8-Triphenyl-2,9-dioxatricyclo[4.3.3.0^{1,6}]dodec-3-en-12-one (**13aa**)*

R_f=0.71 (chloroform); colorless prisms (from chloroform–hexane); mp 155–156 °C; IR (KBr) ν 1749 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.07 (15H, m, arom. H), 5.29 (1H, dd, J=6.1, 2.6 Hz, H-4), 3.36 (1H, d, J=13.2 Hz, H-7), 2.73 (1H, d, J=13.2 Hz, H-7), 2.59 (1H, d, J=14.7 Hz, H-11), 2.43–2.12 (5H, m, H-5, H-10, H-11); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.7 (C=O), 150.1 (C-3), 147.2, 144.8, 134.7 (3C, arom. C), 130.0, 128.2, 128.1, 128.0, 127.9, 127.2, 126.6, 125.7, 125.57, 125.55, 124.69, 124.67 (15C, arom. *C*H), 112.6 (C-1), 92.5 (C-4), 89.7 (C-8), 56.0 (C-6), 45.2 (C-7), 35.2 (C-10), 30.2 (C-11), 23.8 (C-5). Anal. Calcd for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.31; H, 6.06.

*4.3.33. 3,12,12-Triphenyl-2,11-dioxatricyclo[4.4.3.0^{1,6}]-tridec-3-en-7-one (**13ab**)*

R_f=0.62 (chloroform); colorless microcrystals (from ethyl acetate–hexane); mp 169–170 °C; IR (KBr) ν 1711 (C=O);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.47 (4H, m, arom. H), 7.28–7.06 (11H, m, arom. H), 5.13 (1H, dd, J=5.3, 2.8 Hz, H-4), 3.79 (1H, d, J=12.5 Hz, H-13), 2.74 (1H, d, J=12.5 Hz, H-13), 2.54–1.85 (8H, m, H-5, H-8, H-9, H-10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9 (C=O), 149.4 (C-3), 148.8, 145.8, 135.1 (3C, arom. C), 128.0, 127.90, 127.87, 126.6, 126.2, 125.3, 125.2, 124.4 (15C, arom. *C*H), 107.9 (C-1), 90.62, 90.60 (1C, C-4), 87.3 (C-12), 57.9 (C-6), 42.5 (C-13), 36.3 (C-10), 29.6 (C-8), 27.3 (C-5), 19.3 (C-9). Anal. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20. Found: C, 82.14; H, 6.23.

*4.3.34. 9,9-Dimethyl-3,12,12-triphenyl-2,11-dioxatricyclo-[4.4.3.0^{1,6}]tridec-3-en-7-one (**13ac**)*

R_f=0.73 (chloroform); colorless prisms (from chloroform); mp 204–206 °C; IR (KBr) ν 1709 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.00 (15H, m, arom. H), 5.11 (1H, dd, J=5.3, 2.8 Hz, H-4), 4.05 (1H, d, J=12.8 Hz, H-13), 2.63 (1H, d, J=12.8 Hz, H-13), 2.57 (1H, d, J=14.5 Hz, H-10), 2.50 (1H, dd, J=18.4, 2.8 Hz, H-5), 2.37 (1H, dd, J=14.5, 1.8 Hz, H-8), 2.27 (1H, dd, J=18.4, 5.3 Hz, H-5), 2.08 (1H, dd, J=14.5, 1.8 Hz, H-8), 2.03 (1H, d, J=14.5 Hz, H-10), 1.05 (3H, s, CH_3), 1.00 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9 (C=O), 150.1 (C-3), 149.3, 135.1, 132.4 (3C, arom. C), 128.2, 128.1, 127.9, 127.83, 127.78, 126.5, 125.8, 125.5, 124.6, 124.4 (15C, arom. *C*H), 108.1 (C-1), 90.59, 90.55 (1C, C-4), 87.6 (C-12), 57.0 (C-6), 49.3 (C-10), 42.1 (C-8), 41.2 (C-13), 33.1 (*C*H$_3$), 32.4 (C-9), 27.8 (*C*H$_3$), 27.7 (C-5). Anal. Calcd for $C_{31}H_{30}O_3$: C, 82.64; H, 6.71. Found: C, 82.36; H, 6.81.

*4.3.35. 2,3,4,4a,5,6,7,8,9,9a-Decahydro-4a,9a-(12,12-diphenylepoxyethano)xanthen-1-one (**13ad**)*

R_f=0.51 (chloroform); colorless microcrystals (from chloroform–hexane); mp 152.5 °C; IR (KBr) ν 1709 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.42 (4H, m, arom. H), 7.25–7.08 (6H, m, arom. H), 3.73 (1H, d, J=12.5 Hz, H-13), 2.64 (1H, d, J=12.5 Hz, H-13), 2.49–2.33 (2H, m, CH_2), 2.15–1.83 (9H, m, CH_2), 1.63–1.45 (5H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2 (C=O), 148.6, 145.8, 144.2 (3C, C-10a, arom. C), 127.7, 126.5, 126.1, 125.4, 125.3 (10C, arom. *C*H), 106.8 (C-4a), 98.1 (C-8a), 87.0 (C-12), 58.7 (C-9a), 42.8, 36.4, 31.8, 29.8, 27.8, 26.7, 22.7, 19.1 (9C, *C*H$_2$). Anal. Calcd for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 80.93; H, 6.97.

*4.3.36. 1-Hydroxy-5-(3-oxo-3-phenylpropyl)-3,3-diphenyl-2-oxabicyclo[3.3.0]octan-6-one (**14aa**)*

R_f=0.18 (chloroform); colorless oil; IR (KBr) ν 3600–3100 (OH), 1736, 1684 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.89 (2H, m, arom. H), 7.54–7.08 (13H, m, arom. H), 3.60 (1H, br s, O*H*), 3.39 (1H, d, J=12.8 Hz, H-4), 3.24–3.13 (1H, m, Bz–CH_2CH$_2$), 2.98–2.87 (1H, m, Bz–CH_2CH$_2$), 2.68 (1H, d, J=12.8 Hz, H-4), 2.63–1.87 (6H, m, H-7, H-8, Bz–CH$_2$CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.8, 199.5 (2C, C=O), 148.3, 145.4, 136.5 (3C, arom. C), 133.2, 128.5, 128.2, 128.1, 127.0, 126.8, 125.3 (15C, arom. *C*H), 112.4 (C-1), 88.2 (C-3), 61.6 (C-5), 46.2 (C-4), 36.5, 33.5, 31.5, 25.2 (4C, C-7, C-8, Bz–*C*H$_2$*C*H$_2$). FAB HRMS (acetone–NBA) calcd for $C_{28}H_{26}O_4$ 426.1831 (M). Found 426.1805.

*4.3.37. 1-Acetoxy-5-(3-oxo-3-phenylpropyl)-3,3-diphenyl-2-oxabicyclo[3.3.0]octan-6-one (**14aa′**)*

R_f=0.29 (chloroform); colorless oil; IR (KBr) ν 1746, 1688 (C=O), 1236 (Ac); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.92 (2H, m, arom. H), 7.56–7.08 (13H, m, arom. H), 3.52–3.46 (1H, m, CH_2), 3.35 (1H, d, J=12.7 Hz, H-4), 3.24–3.13 (1H, m, Bz–CH_2CH$_2$), 3.04–2.93 (1H, m, Bz–CH_2CH$_2$), 2.83 (1H, d, J=12.7 Hz, H-4), 2.58–1.93 (5H, m, H-7, H-8, Bz–CH$_2$CH_2), 1.68 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.7, 198.9, 169.4 (3C, C=O), 147.7, 145.5, 136.5 (3C, arom. C), 133.2, 128.6, 128.3, 128.19, 128.17, 127.99, 127.96, 127.9, 126.94, 126.90, 126.7, 124.9, 124.8 (15C, arom. *C*H), 114.3 (C-1), 90.0 (C-3), 63.3 (C-5), 45.3 (C-4), 36.0, 33.3, 29.4, 24.5 (4C, C-7, C-8, Bz–*C*H$_2$*C*H$_2$), 21.4 (Ac). FAB MS *m/z* (rel intensity), 468 (3, M), 409 (70), 391 (48), 277 (84), 154 (28), 105 (100), 77 (18), 43 (9).

*4.3.38. 6-Hydroxy-1-(3-oxo-3-phenylpropyl)-8,8-diphenyl-7-oxabicyclo[4.3.0]nonan-2-one (**14ab**)*

R_f=0.40 (chloroform–methanol, 98:2, v/v); colorless microcrystals (from ethyl acetate–hexane); mp 96–98 °C; IR (KBr) ν 3600–3100 (OH), 1714, 1684 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.90 (2H, m, arom. H), 7.56–7.08 (14H, m, O*H*, arom. H), 3.84 (1H, d, J=12.1 Hz, H-9), 2.99–2.89 (1H, m, Bz–CH_2CH$_2$), 2.83–2.75 (1H, m, Bz–CH_2CH$_2$), 2.71 (1H, d, J=12.1 Hz, H-9), 2.48–1.83 (8H, m, H-3, H-4, H-5, Bz–CH$_2$CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3, 199.0 (2C, C=O), 149.7, 146.4, 136.6 (3C, arom. C), 133.1, 128.5, 128.2, 128.0, 127.9, 126.5, 126.3, 125.0, 124.8 (15C, arom. *C*H), 107.1 (C-6), 86.1 (C-8), 63.8 (C-1), 43.2 (C-9), 37.5, 34.3, 32.6 (3C, C-3, C-5, Bz–*C*H$_2$CH$_2$), 26.6 (Bz–CH$_2$*C*H$_2$), 19.3 (C-4). Anal. Calcd for $C_{29}H_{28}O_4 \cdot 2/5H_2O$: C, 77.82; H, 6.44. Found: C, 77.87; H, 6.46.

*4.3.39. 6-Hydroxy-4,4-dimethyl-1-(3-oxo-3-phenylpropyl)-8,8-diphenyl-7-oxabicyclo[4.3.0]nonan-2-one (**14ac**)*

R_f=0.42 (chloroform–methanol, 98:2, v/v); colorless microcrystals (from ethyl acetate); mp 138–139 °C; IR (KBr) ν 3600–3100 (OH), 1707, 1684 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.90 (2H, m, arom. H), 7.57–7.05 (14H, m, O*H*, arom. H), 4.12 (1H, d, J=12.5 Hz, H-9), 3.02–2.91 (1H, m, Bz–CH_2CH$_2$), 2.76–2.65 (1H, m, Bz–CH_2CH$_2$), 2.57 (1H, d, J=12.5 Hz, H-9), 2.51 (1H, d, J=13.8 Hz, H-5), 2.33–1.98 (5H, m, H-3, H-5, Bz–CH$_2$CH_2), 1.07 (3H, s, CH_3), 0.93 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 198.9 (2C, C=O), 151.2, 146.0, 136.6 (3C, arom. C), 133.2, 128.6, 128.3, 128.0, 127.9, 126.4, 126.3, 125.2, 124.3 (15C, arom. *C*H), 107.8 (C-6), 86.8 (C-8), 63.5 (C-1), 50.2 (C-5), 45.0 (C-3), 41.5 (C-9), 34.4 (Bz–*C*H$_2$CH$_2$), 33.3 (*C*H$_3$), 32.1 (C-4), 28.0 (Bz–CH$_2$*C*H$_2$), 27.2 (*C*H$_3$). Anal. Calcd for $C_{31}H_{32}O_4$: C, 79.46; H, 6.88. Found: C, 79.26; H, 6.84.

*4.3.40. Ethyl 6-hydroxy-8,8-diphenyl-7-oxabicyclo[4.3.0]nonan-2-one-1-propionate (**14ae**)*

R_f=0.33 (chloroform–methanol, 98:2, v/v); colorless oil; IR (KBr) ν 3600–3200 (OH), 1732, 1713 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.06 (10H, m, arom. H), 4.09 (2H, q, J=7.1 Hz, O–CH_2CH$_3$), 3.75 (1H, d, J=12.1 Hz, H-9), 2.74 (1H, br s, O*H*), 2.63 (1H, d, J=12.1 Hz, H-9), 2.42–1.80 (10H, m, CH_2×5), 1.20 (3H, t, J=7.1 Hz, O–CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 172.9 (2C, C=O), 149.7, 146.2 (2C, arom. C), 128.0, 127.7, 126.3, 126.2, 124.9, 124.7 (10C, arom. *C*H), 106.9 (C-6), 86.0 (C-8), 63.6 (C-1), 60.4 (O–*C*H$_2$CH$_3$), 42.9, 37.5, 32.4, 30.2, 27.6, 19.2 (6C, *C*H$_2$), 14.0 (O–CH$_2$*C*H$_3$). FAB HRMS (acetone–NBA) calcd for $C_{25}H_{28}O_5$ 408.1937 (M). Found 408.1938.

*4.3.41. Ethyl 3-(4-oxo-2,2-diphenyl-2,3,5,6-tetrahydro-4H-benzofuran-3a-yl)propionate (**15**)*

R_f=0.66 (chloroform–methanol, 98:2, v/v); colorless oil; IR (KBr) ν 1734, 1713 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.17 (10H, m, arom. H), 5.26 (1H, dd, J=7.0, 2.2 Hz, H-7), 4.01 (2H, q, J=7.0 Hz, O–CH_2CH$_3$), 2.98 (1H, d, J=13.6 Hz, H-3), 2.84 (1H, d, J=13.6 Hz, H-3), 2.39–1.95 (8H, m, CH_2×4), 1.17 (3H, t, J=7.0 Hz, O–CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.2, 172.3 (2C, C=O), 156.9 (C-7a), 145.6, 145.3 (2C, arom. C), 128.5, 128.3, 127.19, 127.17, 125.5, 125.0 (10C, arom. *C*H), 93.8 (C-7), 89.3 (C-2), 60.5 (O–*C*H$_2$CH$_3$), 57.2 (C-3a), 41.8, 34.8, 29.5, 28.3, 19.5 (5C, *C*H$_2$), 14.1 (O–CH$_2$*C*H$_3$). FAB HRMS (acetone–NBA) calcd for $C_{25}H_{27}O_4$ 391.1909 (M+1). Found 391.1989.

*4.3.42. 3-Methyl-8,11,11-triphenyl-3-aza-7,12-dioxa-4,5-benzotricyclo[4.3.3.0^{1,6}]dodec-8-en-2-one (**17aa**)*

R_f=0.58 (chloroform); colorless microcrystals (from diethyl ether–hexane); mp 94–95 °C; IR (KBr) ν 1663 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10–8.07 (1H, m, arom. H), 7.59–7.56 (2H, m, arom. H), 7.39–6.93 (16H, m, arom. H), 5.34 (1H, s, H-9), 3.66 (1H, d, J=13.0 Hz, H-10), 3.26 (3H, s, N–CH_3), 3.04 (1H, d, J=13.0 Hz, H-10); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8 (C=O), 155.1 (C-8), 145.4, 144.2, 136.1 (3C, arom. C), 130.2 (arom. *C*H), 129.3 (arom. C), 128.8, 128.0, 127.8, 127.7, 126.9, 126.5, 125.6, 125.4 (arom. *C*H), 123.8 (arom. C), 122.9, 114.3 (arom. *C*H), 112.4 (C-6), 98.70, 98.66 (1C, C-9), 89.2 (C-11), 62.8 (C-1), 50.4 (C-10), 29.3 (N–*C*H$_3$). Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 81.48; H, 5.59; N, 2.82. FAB HRMS (acetone–NBA) calcd for $C_{32}H_{26}NO_3$ 472.1913 (M+1). Found 472.1910.

*4.3.43. 8-Methyl-3,12,12-triphenyl-8-aza-2,11-dioxa-9,10-benzotricyclo[4.4.3.0^{1,6}]tridec-3-en-7-one (**17ab**)*

R_f=0.31 (chloroform); colorless prisms (from diethyl ether–hexane); mp 209 °C; IR (KBr) ν 1672 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77–7.01 (19H, m, arom. H), 5.21 (1H, dd, J=5.3, 2.4 Hz, H-4), 3.78 (1H, d, J=12.5 Hz, H-13), 3.14 (1H, d, J=12.5 Hz, H-13), 3.07 (3H, s, N–CH_3), 2.56 (1H, dd, J=18.5, 5.3 Hz, H-5), 2.15 (1H, dd, J=18.5, 2.4 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6 (C=O), 147.8, 147.6, 145.4, 138.2, 134.3 (5C, arom. C, C-3), 130.6, 128.5, 128.1, 128.0, 127.9, 127.6, 126.6, 125.8, 125.3, 124.1, 123.4 (arom. *C*H), 122.5 (arom. C), 114.6 (arom. *C*H), 102.7 (C-1), 92.9, 92.8 (1C, C-4), 88.5 (C-12), 50.0 (C-6), 45.2 (C-13), 29.7 (N–*C*H$_3$), 26.3 (C-5). Anal. Calcd for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.64; H, 5.73; N, 2.92.

*4.3.44. 3,12,12-Triphenyl-2,8,11-trioxa-9,10-benzotricyclo-[4.4.3.0^{1,6}]tridec-3-en-7-one (**17ac**)*

R_f=0.67 (chloroform); colorless microcrystals (from diethyl ether–hexane); mp 159 °C; IR (KBr) ν 1769 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73–7.04 (19H, m, arom. H), 5.18 (1H, dd, J=5.3, 2.6 Hz, H-4), 3.80 (1H, d, J=12.7 Hz, H-13), 3.21 (1H, d, J=12.7 Hz, H-13), 2.60 (1H, dd, J=18.5, 5.3 Hz, H-5), 2.36 (1H, dd, J=18.5, 2.6 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4 (C=O), 149.6, 148.3, 147.5, 145.0, 134.0 (5C, arom. C, C-3), 131.5, 128.3, 128.2, 128.1, 128.0, 127.0, 126.7, 125.6, 125.2, 125.0, 124.2 (arom. *C*H), 120.5 (arom. C), 116.9 (arom. *C*H), 101.6 (C-1), 92.0, 91.9 (1C, C-4), 88.8 (C-12), 50.6 (C-6), 44.4 (C-13), 26.3 (C-5). Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 81.37; H, 5.17.

*4.3.45. 3-Methyl-8,11,11-triphenyl-2-aza-8,9-dioxa-3,4-benzotricyclo[4.3.3.0^{1,6}]dodec-7-en-5-one (**18**)*

R_f=0.38 (chloroform); colorless microcrystals (from diethyl ether–hexane); mp 237–238 °C; IR (KBr) ν 1678 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.11 (19H, m, arom. H), 5.61 (1H, s, H-7), 3.35 (3H, s, N–CH_3), 3.21 (1H, d, J=14.0 Hz, H-12), 3.03 (1H, d, J=14.0 Hz, H-12); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (C=O), 152.5 (C-8), 144.1, 142.3, 142.1 (3C, arom. C), 135.0 (arom. *C*H), 134.9 (arom. C), 131.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.5, 126.1, 125.9, 125.2, 123.1 (17C, arom. *C*H), 122.0 (arom. C), 114.7 (C-1), 114.5 (arom. *C*H), 94.2 (C-9), 81.2 (C-11), 57.6 (C-6), 40.6 (C-12), 30.6 (N–*C*H$_3$). Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 81.50; H, 5.37; N, 2.95. FAB HRMS (acetone–NBA) calcd for $C_{32}H_{26}NO_3$ 472.1913 (M+1). Found 472.1917.

*4.3.46. 3-(2-Hydroxy-2,2-diphenylethyl)-1-methyl-3-(2-oxo-2-phenylethyl)-1H-quinoline-2,4-dione (**19**)*

R_f=0.27 (chloroform); colorless prisms (from ethyl acetate–hexane); mp 180–183 °C; IR (KBr) ν 3600–3150 (OH), 1682, 1638 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88–7.63 (3H, m, arom. H), 7.60–7.01 (16H, m, arom. H), 4.41 (1H, d, J=17.8 Hz, Bz–CH_2), 4.10 (1H, d, J=17.8 Hz, Bz–CH_2), 3.87 (1H, br s, O*H*), 3.08 (1H, d, J=14.5 Hz, CH_2), 3.00 (1H, d, J=14.5 Hz, CH_2), 2.89 (3H, s, N–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6, 196.3, 173.0 (3C, C=O), 146.1, 142.6 (2C, arom. C), 135.4 (2C, arom. C, arom. *C*H), 133.5, 128.4 (arom. *C*H), 128.3 (2C, arom. C, arom. *C*H), 127.94, 127.88, 126.8, 126.7, 125.4, 125.2, 122.8 (arom. *C*H), 120.9 (arom. C), 114.7 (arom. *C*H), 77.1 (Ph$_2$>*C*), 54.8 (C-3), 51.0 (Bz–*C*H$_2$), 49.0 (*C*H$_2$), 29.3 (N–*C*H$_3$). Anal. Calcd for $C_{32}H_{27}NO_4$: C, 78.51; H, 5.56; N, 2.86. Found: C, 78.33; H, 5.64; N, 2.72. FAB HRMS (acetone–NBA) calcd for $C_{32}H_{27}NO_4$ 489.1940 (M). Found 489.1941.

*4.3.47. 3-(2,2-Diphenylvinyl)-1-methyl-3-(2-oxo-2-phenylethyl)-1H-quinoline-2,4-dione (**20aa**)*

R_f=0.49 (chloroform); colorless prisms (from hexane); mp 169 °C; IR (KBr) ν 1684, 1655 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.83 (3H, m, arom. H), 7.58–7.50 (2H, m, arom. H), 7.42–6.90 (14H, m, arom. H), 6.07 (1H, s, Ph_2>C=C*H*), 4.40 (1H, d, J=17.6 Hz, Bz–CH_2), 4.28 (1H, d, J=17.6 Hz, Bz–CH_2), 3.02 (3H, s, N–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 193.9, 171.0 (3C, C=O), 145.1 (Ph_2>*C*), 143.1, 142.0, 137.3 (3C, arom. C), 135.5, 135.4 (arom. *C*H), 133.5 (arom. C), 129.7, 128.4, 128.3, 128.0, 127.8, 127.6, 127.5, 127.0, 126.2 (arom. *C*H), 126.2 (Ph_2>C=*C*H), 122.5 (arom. *C*H), 120.7 (arom. C), 115.0 (arom. *C*H), 58.8 (C-3), 50.1 (Bz–*C*H_2), 29.5 (N–*C*H_3). Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 81.58; H, 5.36; N, 2.98. FAB HRMS (acetone–NBA) calcd for $C_{32}H_{26}NO_3$ 472.1913 (M+1). Found 472.1937.

*4.3.48. 3-(2,2-Diphenylvinyl)-1-methyl-3-(3-oxo-3-phenylpropyl)-1H-quinoline-2,4-dione (**20ab**)*

R_f=0.42 (chloroform–methanol, 98:2, v/v); colorless microcrystals (from ethyl acetate–hexane); mp 139–140 °C; IR (KBr) ν 1684, 1645 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–6.84 (19H, m, arom. H), 6.40 (1H, s, Ph_2>C=C*H*), 3.08 (3H, s, N–CH_3), 2.97–2.92 (2H, m, Bz–CH_2CH$_2$), 2.75–2.69 (2H, m, Bz–CH$_2$CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 196.2, 172.0 (3C, C=O), 144.3, 142.7, 140.9, 138.3, 136.4 (5C, arom. C, Ph_2>*C*), 135.9 (arom. *C*H), 133.0 (Ph_2>C=*C*H), 130.7, 130.0, 128.5, 128.0, 127.6, 127.4, 127.1, 122.7 (arom. *C*H), 120.3 (arom. C), 114.6 (arom. *C*H), 59.8 (C-3), 35.8 (Bz–*C*H$_2$CH$_2$), 33.3 (Bz–CH$_2$*C*H$_2$), 29.3 (N–*C*H_3). Anal. Calcd for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.93; H, 5.63; N, 2.92.

*4.3.49. 9b-Hydroxy-5-methyl-3a-(3-oxo-3-phenylpropyl)-2,2-diphenyl-3,3a,5,9b-tetrahydro-2H-furo[3,2-c]quinolin-4-one (**21**)*

R_f=0.33 (chloroform–methanol, 98:2, v/v); colorless prisms (from ethyl acetate); mp 211–212 °C; IR (KBr) ν 3600–3100 (OH), 1680, 1641 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–6.92 (19H, m, arom. H), 3.77 (1H, d, J=11.7 Hz, H-3), 3.76 (1H, br s, O*H*), 3.15 (1H, d, J=11.7 Hz, H-3), 3.09–2.67 (2H, m, Bz–CH_2CH$_2$), 2.94 (3H, s, N–CH_3), 2.28–2.11 (2H, m, Bz–CH$_2$CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 170.3 (2C, C=O), 147.9, 145.6, 137.7, 136.1 (4C, arom. C), 133.0, 130.1, 128.3, 127.8, 127.6, 126.8, 126.4, 126.2, 125.5 (arom. *C*H), 125.2 (arom. C), 125.0, 123.3, 114.5 (arom. *C*H), 101.6 (C-9b), 87.4 (C-2), 57.8 (C-3a), 48.1 (C-3), 34.0 (Bz–*C*H$_2$CH$_2$), 29.9 (N–*C*H_3), 26.1 (Bz–CH$_2$*C*H$_2$). Anal. Calcd for $C_{33}H_{29}NO_4$: C, 78.71; H, 5.80; N, 2.78. Found: C, 78.86; H, 5.88; N, 2.74.

*4.4. Lewis acid-induced cyclization of propellane intermediates **14aa**, **14ab**, **14ac**, and **21***

The intermediates **14aa**, **14ab**, **14ac**, or **21** (0.1 mmol) and dry THF (2 mL) were placed in a 30 mL flask. The appropriate Lewis acid ($AlCl_3$ or $EtAlCl_2$ in hexanes) (0.4 mmol) was added to the reaction mixture, which was then stirred at room temperature. The mixture was further heated under reflux until the starting material was completely consumed as necessary. The resulting solution was quenched with water (10 mL) and extracted with chloroform (5 mL×3). The combined chloroform extracts were dried over anhydrous $MgSO_4$ and concentrated to dryness under vacuum. The obtained crude products were purified by column chromatography on silica gel while eluting with chloroform, giving the desired propellanes **13aa**, **13ab**, **13ac**, and **17ab**.

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Supplementary data

The result for the reaction of alkenes **1a–e** with **2a–h** except for the reaction of **1b**,**c** with **2a** without a 10-min heating after finishing the oxidation (Scheme 1-1 and Table 1-1) (1 page), and the experimental procedures (1 page), spectroscopic and characterization data for **2** and the rest of the compounds described in this paper (11 pages). The spectral data of dioxapropellanes **3aa**, **3ah**, trioxapropellanes **4aa**, **4ah**, the by-product acetates **5**, **5ah**, the bicycloacetate **6ah**, and dioxapropellane **13ab** produced by Lewis acid-induced cyclization (45 pages). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.12.017.

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