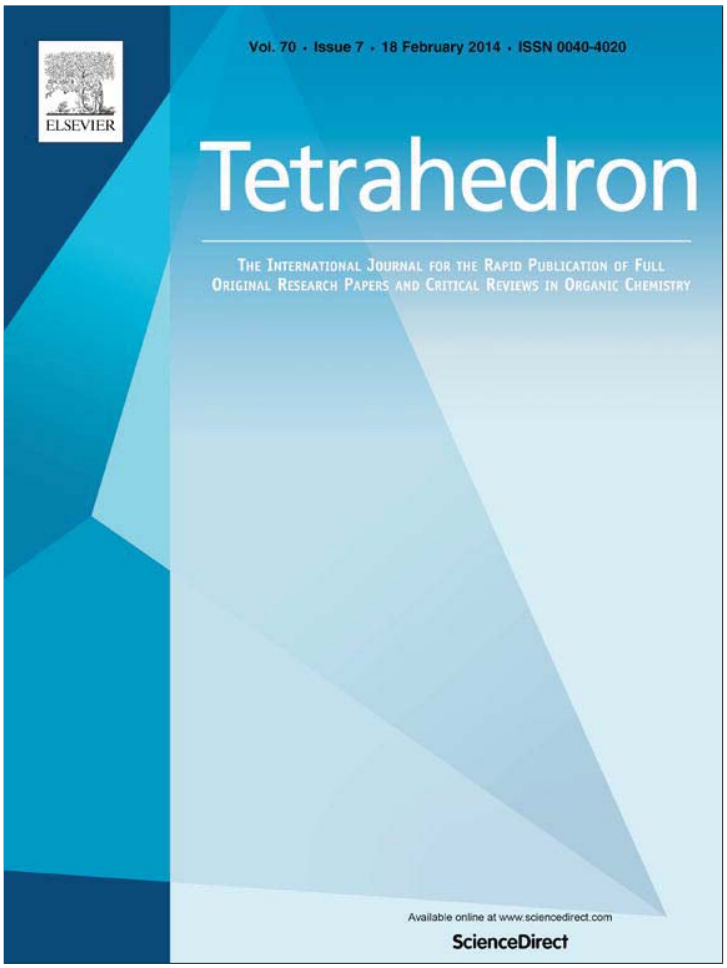

Tetrahedron 70 (2014) 1437–1450

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Mn(III)-based reaction of alkenes with quinolinones. Formation of peroxyquinolinones and quinoline-related derivatives

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ARTICLE INFO

Article history:
Received 19 September 2013
Received in revised form 30 December 2013
Accepted 1 January 2014
Available online 10 January 2014

Keywords:
Hydroperoxides
Endoperoxides
Quinolines
Propellanes
Aerobic oxidation
Mn(III)
Oxidation

ABSTRACT

The reactions of 1,1-disubstituted alkenes with 4-hydroxyquinolin-2(1*H*)-ones under both Mn(III)-catalyzed aerobic oxidation conditions at room temperature and Mn(III)-mediated oxidation conditions at reflux temperature are described. The Mn(III)-catalyzed aerobic oxidation afforded bis(hydroperoxyethyl)quinolinones and azatrioxa[4.4.3]propellanes, while the oxidation with $Mn(OAc)_3 \cdot 2H_2O$ produced furo[3,2-*c*]quinolin-4-one analogues. The existence of a substituent at the 3-position of the 4-hydroxyquinolin-2(1*H*)-ones prevented a double reaction with the alkenes, and (endoperoxy)quinolinones and/or (hydroperoxyethyl)quinolinones were obtained under the Mn(III)-catalyzed aerobic conditions, while furo[3,2-*c*]quinolinone hemiacetals and vinylquinolinones were selectively produced under the Mn(III)-mediated oxidation conditions depending on the reaction temperature and times. Cyclic assembly of quinolinone-related 1,3-dicarbonyl compounds such as dihydropyridinones, pyranones, and dimedone derivatives was also examined under elevated temperature conditions.

1. Introduction

Quinoline alkaloids are some of the most important natural products and the synthesis of heterocycles containing the quinoline core is interesting from the standpoint of searching for new biologically active compounds.[1,2] Mn(III)-assisted oxidation is one of the useful tools for formation of the carbon–carbon bond to a heterocyclic ring such as addition and substitution.[3,4] For example, the aerobic oxidation[5] of pyrazolidine-3,5-diones,[6] tetronic acids,[7] and tetramic acids[8] using $Mn(OAc)_3 \cdot 2H_2O$ as a catalyst in the presence of alkenes gave hydroperoxides and endoperoxides such as bis(hydroperoxyethyl)pyrazolidinediones, 1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-ones, and 8-aza-1-hydroxy-2,3-dioxabicyclo[4.3.0]nonan-7-ones, while the direct hydroperoxidation to a heterocyclic ring occurred by a similar reaction using substituted cyclic diamides in the absence of alkenes.[9] On the other hand, the oxidation of alkenes with the Mn(III)-enolate complex as an oxidant caused oxidative cyclization, producing dihydrofurans[10] and lactones.[11] In order to construct a complex quinoline core, 4-hydroxyquinolin-2(1*H*)-ones are a suitable reagent for the Mn(III)-based peroxidation and dihydrofuranation.[12] We initially demonstrated the Mn(III)-catalyzed aerobic oxidation of 1,1-diarylethenes in the presence of the 4-hydroxyquinolinones at room temperature to produce (hydroperoxyethyl)quinoline-diones and [4.4.3]propellane-type endoperoxides.[13] A similar reaction using a stoichiometric amount of Mn(III) at elevated temperature formed furo[3,2-*c*]quinolin-4(2*H*)-ones and 3-vinylquinoline-2,4-diones.[14] In this paper, we describe the results of the oxidation of a mixture of 1,1-disubstituted alkenes and 4-hydroxyquinolinones, and the synthetic application of the dihydrofuranation using the quinolinones and related 1,3-dicarbonyl compounds together with the full experimental results of these reactions.

2. Results and discussion

2.1. Aerobic oxidation of a mixture of alkenes 1 and 4-hydroxyquinolin-2(1*H*)-ones 2 (X=H)[13]

Based on our study of the Mn(III)-catalyzed peroxidation,[5a] it was predicted that the reaction of 1,1-diphenylethene **1** (Ar^1=Ar^2=Ph) with 1-methyl-4-hydroxyquinolin-2(1*H*)-one **2** (X=H, R=Me) must form an endoperoxide such as 4,4a,6,10b-tetrahydro-10b-hydroxy-6-methyl-3,3-diphenyl-1,2-dioxino[4,3-*c*]quinolin-5(3*H*)-one (Scheme 1). The reaction did not occur in the

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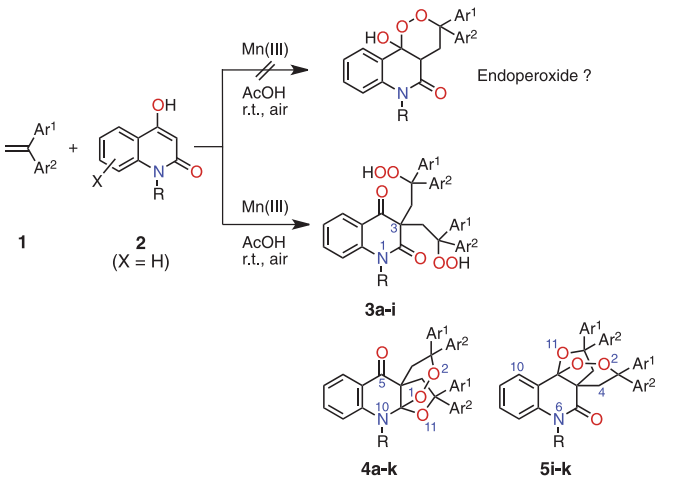
0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.01.013



Scheme 1. Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and quinolinones **2** (X=H).

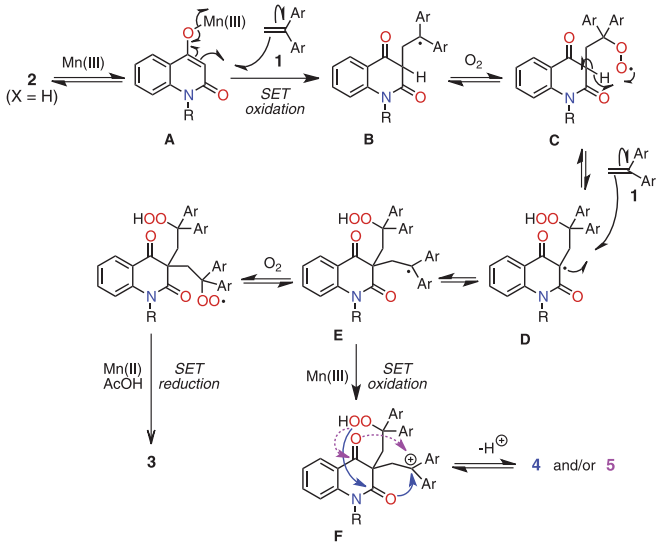
absence of $Mn(OAc)_3$ (Table 1, entry 1), and the use of 1 mmol of $Mn(OAc)_3$ gave an intractable mixture (entry 2). Surprisingly, a bis(hydroperoxide) **3a** was isolated from the reaction mixture when a catalytic amount of $Mn(OAc)_3$ was used in air (Scheme 1 and Table 1, entry 3). In order to prevent the double substitution, the reaction was carried out using 2 equiv of quinolinone **2** toward the alkene **1** (entries 4–6). However, the reaction resulted in the bis(hydroperoxide) **3a** as an isolable product, and the monohydroperoxide and the desired endoperoxide as well as **1** unchanged were not obtained. In addition, use of excess amount of **1** toward quinolinone **2** caused the reaction complicated. Another combination of alkenes **1** (Ar^1=Ar^2=4-ClC_6H_4, 4-Me-C_6H_4) and quinolinones **2** (X=H, R=Et, Bn, H, Me) also underwent the aerobic oxidation to afford similar bis(hydroperoxide)s **3b**–**h** (entries 7–13). When a combination of the alkene **1** (Ar^1=Ar^2=Ph) and the quinolinone **2** (X=H, R=Et) was used, the best yield of bis(hydroperoxide) **3d** was achieved (entry 9). In order to search for other products, we scrutinized the reaction and found another product, [4.4.3]propellanes **4b**–**h** (entries 6–13). The structure of bis(hydroperoxide)s **3** and [4.4.3]propellanes **4** was determined by spectroscopic methods as well as X-ray crystallography for a single crystal of bis(hydroperoxide) **3b** and [4.4.3]propellane **4a** (see Supplementary data).[13] Although it is known that the aerobic oxidation of cyclic diamides in the presence of alkenes does not give the corresponding endoperoxides, but bis(hydroperoxide)s,[9] it is remarkable that the dual hydroperoxidation was favored even using cyclic keto-amides such as **2** (enol form of quinoline-2,4-diones). In addition, it is surprising that the propellane **4**, which was cyclized at the amide carbonyl group, was also isolated as a byproduct.[12d] The reaction using **2** (R=X=H) with no N-protection actually gave the bis(hydroperoxide) **3h** with a trace amount (entry 13). However, most of the bis(hydroperoxide) **3h** seemed to be further oxidized under the conditions and we could not separate the fragments. When the reaction using 2-(1-phenylvinyl)thiophene **1** (Ar^1=Ph, Ar^2=2-thienyl)[10f,i,o] was carried out under similar conditions, the reaction was rather sluggish and gave the corresponding propellane **4i** together with another propellane **5i** as an inseparable stereoisomeric mixture (entry 14). The propellane **5i** was distinguishable from the other propellane **4i** based on the absence of the ketocarbonyl carbon in the ^{13}C NMR spectrum. The yield was improved by increasing the amount of thiophene **1** and oxidant (entries 15 and 16). The reaction of other 2-(1-arylvinyl) thiophenes **1** (Ar^1=4-F-C_6H_4 and 4-Me-C_6H_4, Ar^2=2-thienyl) also led to a similar result (entries 17 and 18).

In order to investigate the interconversion between the bis(hydroperoxide) **3** and the propellane **4** during the reaction, the bis(hydroperoxide) **3a** (R=Me, Ar^1=Ar^2=Ph) and the propellane **4a** (R=Me, Ar^1=Ar^2=Ph), respectively, were then treated both in the absence and presence of $Mn(OAc)_3$ (see Experimental section). As a result, it was confirmed that the bis(hydroperoxide) **3a** and the propellane **4a** were not converted into each other during the reaction. Therefore, we proposed the aerobic oxidation pathway as shown in Scheme 2.[6,7] The Mn(III)-enolate complex **A** produced in situ by the reaction of $Mn(OAc)_3$ with quinolinone **2** (X=H) undergoes single-electron transfer (SET) oxidation with the alkene **1** to form the corresponding tertiary radical **B**, which captures the dissolved molecular oxygen followed by hydrogen abstraction, affording the monohydroperoxyethyl radical **D**.[6,7] The radical intermediate **D** undergoes a similar aerobic oxidation via an alkyl radical intermediate **E** to furnish the bis(hydroperoxide)s **3**. The radical intermediate **E** would also be oxidized by the oxidant to produce the corresponding cation **F**, which undergoes double cyclization to afford the propellanes **4** and/or **5**. The use of an excess amount of the catalyst accelerated the oxidation of the tertiary radical **E**, which resulted in the exclusive production of the propellanes **4i**–**k** and **5i**–**k** (Table 1, entries 15–18).

Table 1
Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and quinolinones **2** (X=H)[a]

Entry	Alkene **1**		Quinolinone **2**/R	Molar ratio of **1**/**2**/$Mn(OAc)_3 \cdot 2H_2O$	Time/h	Product (yield/%)[b]		
	Ar^1	Ar^2						
1	Ph	Ph	Me	1:1:0	4	No reaction		
2	Ph	Ph	Me	1:2:1	4	Intractable mixture		
3	Ph	Ph	Me	2:1:0.5	12	**3a** (32)		
4	Ph	Ph	Me	1:2:0.1	4	**3a** (29)		
5	Ph	Ph	Me	1:2:0.5	12	**3a** (43)		
6	Ph	Ph	Me	1:2:0.5	4	**3a** (71)	**4a** (13)	
7	4-Cl-C_6H_4	4-Cl-C_6H_4	Me	1:2:0.5	12	**3b** (76)	**4b** (10)	
8	4-Me-C_6H_4	4-Me-C_6H_4	Me	1:2:0.5	4	**3c** (59)	**4c** (10)	
9	Ph	Ph	Et	1:2:0.5	15	**3d** (91)	**4d** (5)	
10	Ph	Ph	Bn	1:2:0.5	12	**3e** (52)	**4e** (Trace)	
11	4-Cl-C_6H_4	4-Cl-C_6H_4	Bn	1:2:0.5	24	**3f** (48)	**4f** (Trace)	
12	4-Me-C_6H_4	4-Me-C_6H_4	Bn	1:2:0.5	4	**3g** (44)	**4g** (Trace)	
13	Ph	Ph	H	1:2:0.5	4	**3h** (trace)	**4h** (34)	
14	Ph	2-Thienyl	Me	2:1:0.5	18	**3i** (trace)	**4i** (7)	**5i** (28)
15	Ph	2-Thienyl	Me	2:1:3	12		**4i** (39)	**5i** (27)
16	Ph	2-Thienyl	Me	2:1:3	12		**4i** (22)	**5i** (39)
17	4-F-C_6H_4	2-Thienyl	Me	2:1:3	12		**4j** (22)	**5j** (32)
18	4-Me-C_6H_4	2-Thienyl	Me	2:1:3	18		**4k** (22)	**5k** (47)

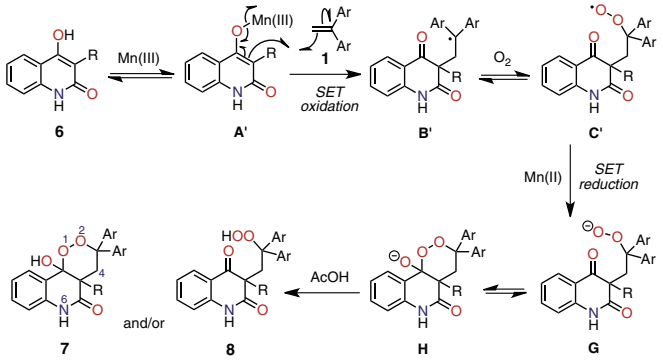
[a] The reaction of alkene **1** (1 mmol) with quinoline **2** (2 mmol) was carried out in glacial acetic acid (25 mL) at room temperature in air.
[b] The yield was based on the amount of the alkene **1** used.



Scheme 2. Mn(III)-based aerobic oxidation pathway for the formation of **3**, **4**, and/or **5**.

2.2. Aerobic oxidation of a mixture of alkenes 1 and 3-substituted quinolinones 6[13]

In order to investigate the possibility of the synthesis of endoperoxides, we designed the reaction using 3-substituted quinolinones **6** (Scheme 3). When a substituent is present at the 3-position of the 2-hydroxyquinolinones **2**, the SET reduction of the peroxy radical intermediate **C′** would preferentially proceed because the intramolecular hydrogen abstraction, such as the peroxy radical **C** in Scheme 2, could not occur and the formation of endoperoxides **7** or monohydroperoxides **8** would be expected (Scheme 3). The reaction of 3-methylquinolinone **6** (R=Me) was then carried out under similar aerobic oxidation conditions. The alkene **1** was completely consumed and the desired endoperoxide **7a** was obtained (Table 2, entry 1). However, **7a** seemed to interconvert into



Scheme 3. Mn(III)-based aerobic oxidation of a mixture of substituted ethenes **1** and quinolinones **6**.

the corresponding hydroperoxide **8a** (R=Me, Ar=Ph) even in the NMR time scale because the methyl and methylene carbons were unclear in the ^{13}C NMR spectrum (see Supplementary data). In fact, for the quinolinones **6** bearing a bulky substituent, such as the propyl, butyl, and phenyl group, hydroperoxides **8b**–**d** were predominantly produced along with the endoperoxides **7b**–**d** (entries 2–4).[15] Since it was difficult to separate endoperoxides **7** and hydroperoxides **8** by chromatographic separation, the product yield was calculated based on the crude ^{1}H NMR spectrum as shown in Table 2. The cyclization might be difficult because the steric repulsion would exist between the diphenyl group and the bulky R group or quinolinone skeleton in the transition state of the conversion of **G** into **H** as well as the intermediate **H** itself. In addition, the use of alkene **1** (Ar=4-MeC$_6$H$_4$) also led to the formation of the hydroperoxide **8f** as the major product (entry 6). Although the tendency was also observed for the reaction of tetronic acid with **1** (Ar=4-MeC$_6$H$_4$), the reason was not clear.[7] In either event, the peroxy anion **G** did not cyclize at the amide carbonyl group probably due to the weak electrophilicity of the amide carbonyl carbon.

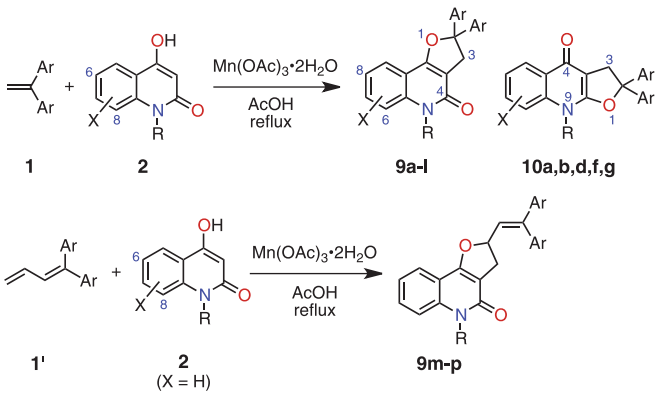
2.3. Mn(III)-mediated oxidation of alkenes in the presence of 4-hydroxyquinolin-2(1*H*)-ones and other related compounds[14]

4-Hydroxyquinolin-2(1*H*)-ones **2** as a reagent are very good candidates not only as a radical source in the Mn(III)-mediated oxidation,[3] but also as a starting material for the synthesis of quinolinone alkaloids such as atanine, araliopsine, and isoplatydesmine.[10c] The 1,3-dicarbonyl compounds, such as 2,4-pentanedione, malonic acid, malonate esters, acetic anhydride, malonamides, and 3-oxobutanoates, undergo oxidative cyclization with alkene using Mn(OAc)$_3$·2H$_2$O at elevated temperature to produce dihydrofurans,[10] spirolactones,[11a,b] γ-lactones,[11c,e–g] lactams,[4c,11h–j] and dihydroquinolinones.[4d] We then applied the reaction to a combination of alkenes **1** and 4-hydroxyquinolinones **2**, and obtained the desired thermodynamically stable angular products, 3,5-dihydrofuro[3,2-*c*]quinolin-4-ones **9**, along with a small amount of linear byproducts, i.e., 3,9-dihydrofuro[2,3-*b*]quinolin-4-ones **10** (upper part in Scheme 4 and Table 3).[10c,14] Since the use of stoichiometric amount of Mn(OAc)$_3$·2H$_2$O (2 equiv) led to the moderate yield of the product **9a** (R=Me, X=H, Ar=Ph) (Table 3, entry 1), an excess amount of the oxidant was necessary to improve the product yield (entry 2). Although other combinations of **1** and **2** also gave a similar result (entries 3–13), the product yield from the quinolinones **2** bearing a substituent at the 6-position was not improved (entries 9 and 11). The reaction of conjugated butadienes **1′** with quinolinones **2** is quite interesting (lower part in Scheme 4). The 1,4-addition did not occur but 1,2-addition, giving vinyl-substituted dihydrofuroquinolinones **9m**–**p** (entries 14–17) similar to copper-mediated reaction of 2,2-dibromodimedone with conjugated dienes.[16]

Table 2
Mn(III)-based aerobic oxidation of a mixture of 1,1-disubstituted ethenes **1** and 3-substituted quinolinones **6**[a]

Entry	Alkene **1**	Qunolinone **6**	Molar ratio of **1**/**6**/Mn(OAc)$_3$·2H$_2$O	Time/h	Product (yield/%)[b]	
	Ar	R				
1	Ph	Me	1:2:0.5	15	**7a** (89)	
2	Ph	Pr	1:2:0.5	18	**7b** (22)	**8b** (60)[c]
3	Ph	Bu	1:2:0.5	15	**7c** (24)	**8c** (52)[c]
4	Ph	Ph	1:2:0.5	15	**7d** (32)	**8d** (43)[c]
5	4-Cl-C$_6$H$_4$	Me	1:2:0.5	18	**7e** (88)	
6	4-Me-C$_6$H$_4$	Me	1:2:0.5	15	**7f** (38)	**8f** (58)[c]

[a] The reaction was carried out at room temperature in air.
[b] The yield was based on the amount of the alkene **1** used.
[c] The yield was calculated by crude NMR analysis.



Scheme 4. Mn(III)-mediated oxidation of substituted ethenes **1** and **1′** in the presence of quinolinones **2**.

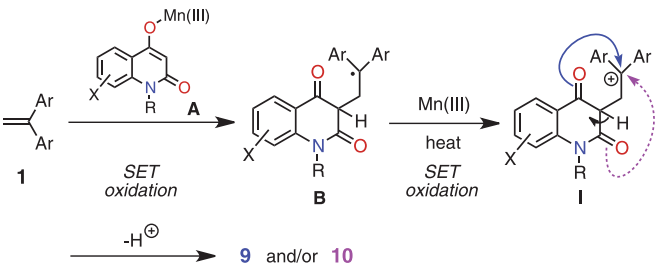
Gratifyingly, the 4-hydroxyquinolinone analogue,[14] such as 4-hydroxy-5,6,7,8-tetrahydroquinolin-2(1*H*)-one (**11**), 1-benzyl-4-hydroxy-5,6-dihydropyridin-2(1*H*)-one (**13**),[4a] 4-hydroxy-2*H*-chromen-2-one (**15**),[10h] and 4-hydroxy-6-methyl-2*H*-pyran-2-one (**17**) also underwent the oxidative cyclization with alkenes **1** to afford the corresponding 2,3-dihydrofuro[3,2-*c*]pyridin-4-ones **12**, **14** and furo[3,2-*c*]pyran-4-ones **16a**–**c**, **18** in moderate to high yields (Table 4, entries 1–6). The cyclization only took place at the enolic ketocarbonyl group, and no products cyclized at the amide and ester carbonyl groups were isolated. Dimedones **19** and **21** were also subjected to the reaction with butadienes **2′** and the corresponding benzofuran-4(5*H*)-ones **20a**–**c**[17] and propellane **22**[12] were obtained (Table 4, entries 7–10). In this case, the reaction with butadienes **1′** led to 1,2-addition similar to the reaction of **1′** with quinolinone **2** in Scheme 4.

Table 3
Mn(III)-mediated oxidation of substituted ethenes **1** and **1′** in the presence of quinolinones **2**[a]

Entry	Alkene **1**	Quinolinone **2**		**1**/**2**/$Mn(OAc)_3 \cdot 2H_2O$	Time/min	Product (yield/%)[b]	
	Ar	R	X				
1	**1**: Ph	Me	H	1:1.5:2	2	**9a** (60)	**10a** (4)
2	**1**: Ph	Me	H	1:2:3	3	**9a** (87)	**10a** (7)
3	**1**: Ph	Et	H	1:2:3	1.5	**9b** (73)	**10b** (trace)
4	**1**: Ph	Pr	H	1:2:3	1.5	**9c** (76)	
5	**1**: Ph	Bn	H	1:2:3	3	**9d** (85)	**10d** (Trace)
6	**1**: Ph	H	H	1:2:3	2	**9e** (73)	
7	**1**: 4-Cl-C_6H_4	Me	H	1:2:3	3	**9f** (87)	**10f** (12)
8	**1**: 4-Me-C_6H_4	Me	H	1:2:3	5	**9g** (93)	**10g** (Trace)
9	**1**: Ph	H	6-Me	1:2:3	30	**9h** (44)	
10	**1**: Ph	H	8-Me	1:2:3	3	**9i** (67)	
11	**1**: Ph	H	6-Cl	1:2:3	4	**9j** (58)	
12	**1**: Ph	H	8-Cl	1:2:3	3	**9k** (98)	
13	**1**: Ph	H	6-F	1:2:3	30	**9l** (74)	
14	**1′**: Ph	Me	H	1:1:3	2	**9m** (71)	
15	**1′**: 4-F-C_6H_4	Me	H	1:1:3	3	**9n** (58)	
16	**1′**: 4-Cl-C_6H_4	Me	H	1:1:3	4	**9o** (69)	
17	**1′**: 4-Me-C_6H_4	Me	H	1:1:3	2	**9p** (71)	

[a] The reaction was carried out in glacial acetic acid at reflux temperature in air.
[b] The yield was based on the amount of the alkene **1** or **1′** used.

The mechanism for the formation of **9** and **10** has been reported by Parsons et al.[10c] 1,1-Diarylethene **2** should be oxidized by the Mn(III)-enolate complex **A** to give the expected tertiary carbon radical **B**, which underwent the SET oxidation under the conditions to produce the tertiary cation **I** (Scheme 5). Although Parsons reported the product yield of **9a** and **10a** as 39% and 41%, respectively,[10c] the reaction conditions (*heat at 60 °C* in an ultrasonic bath in the presence of $KMnO_4$ as the co-oxidant) are different from those of ours (*heat under reflux*) (compared to Table 3, entry 2), therefore, it is obvious that the cyclization is prone to occur at the enolic ketocarbonyl group in the cation **I** and a thermodynamically more stable angular product **9** would be exclusively produced in our case.

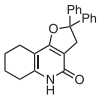
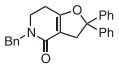
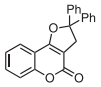
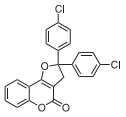
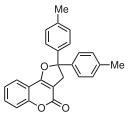
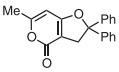
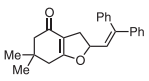
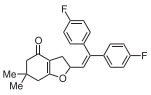
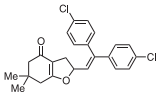
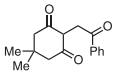
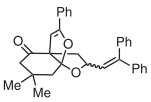


Scheme 5. Reaction pathway for the formation of **9** and/or **10**.

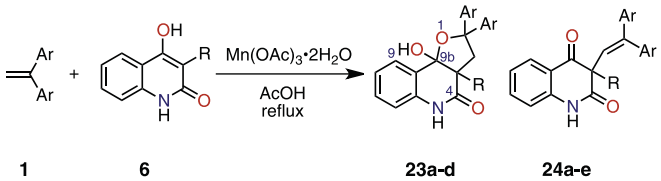
2.4. Mn(III)-mediated oxidation of a mixture of alkenes 2 and 3-substituted quinolinones 6[14]

We were next interested in the Mn(III)-mediated oxidation of quinolinones having a substituent at the 3-position since the deprotonation could not occur at the intermediate cation **I** stage in Scheme 5. The oxidation of a mixture of alkene **1** (Ar=Ph) and 3-substituted quinolinone **6** (R=Me) with $Mn(OAc)_3 \cdot 2H_2O$ was then carried out at the reflux temperature. After 1.5 min, the dark-brown color of the reaction mixture turned transparent and we recognized the complete consumption of the oxidant, and the absence of the oxidant was finally confirmed by a KI-starch test paper. After the usual work-up, furo[3,2-*c*]quinolinone hemiacetal **23a** was obtained along with the vinyl-substituted quinolinone **24a** (Scheme 6 and Table 5, entry 1). Since the hemiacetal **23a** might be unstable under the high temperature conditions, an additional heating for 1 min was conducted after the oxidation. As a result, we found that the yield of **23a** decreased and that of **24a** increased (entry 2). Further additional heating led to only the production of **24a** (entry 3), and the oxidation at 80 °C for 24 h quantitatively gave **24a** (entry 4). These results suggested that the pathway of the hemiacetal **23a** and the vinyl-substituted quinolinone **24a** was in equilibrium under the stated oxidation conditions and the additional heating after the oxidation resulted in the thermodynamically stable **24a** (Scheme 7). Interestingly, the use of $Cu(OAc)_2$ as a co-oxidant[3c] at

Table 4
Mn(III)-mediated oxidation of substituted ethenes **1** and **1′** in the presence of quinolinone-related compounds[a]

Entry	Alkene **1** or **1′**/Ar	Reagent	Time/min	Product (yield/%)[b]
1	**1**: Ph	 **11**	1	 **12** (53)
2	**1**: Ph	 **13**	1	 **14** (52)
3	**1**: Ph	 **15**	5	 **16a** (89)
4	**1**: 4-Cl-C_6H_4	**15**	2	 **16b** (87)
5	**1**: 4-Me-C_6H_4	**15**	4	 **16c** (82)
6	**1**: Ph	 **17**	1	 **18** (56)
7	**1′**: Ph	 **19**	1	 **20a** (78)
8	**1′**: 4-F-C_6H_4	**19**	1	 **20b** (55)
9	**1′**: 4-Cl-C_6H_4	**19**	1	 **20c** (63)
10[c]	**1′**: Ph	 **21**	1	 **22** (58)[d]

[a] The reaction mixture was heated under reflux in air at the molar ratio of alkene **1** or **1′**/reagent/$Mn(OAc)_3 \cdot 2H_2O$=1:2:3.
[b] The yield was based on the amount of the alkene **1** or **1′** used.
[c] The molar ratio of the alkene **1′**/reagent **21**/$Mn(OAc)_3 \cdot 2H_2O$=1:1:2.
[d] A 7:1 diastereomixture based on the ^1H NMR spectrum.



1 **6** **23a-d** **24a-e**

Scheme 6. Mn(III)-mediated oxidation of a mixture of 1,1-disubstituted ethenes **1** and 3-substituted quinolinones **6**.

23 °C led to the exclusive production of the hemiacetal **23a** (entry 5).

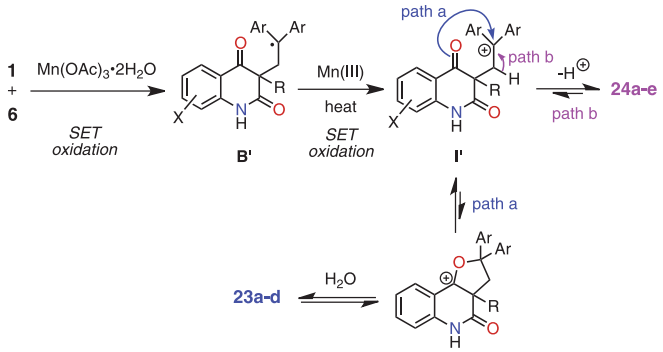
3. Conclusions

We obtained various type of quinolinone derivatives from the simple Mn(III)-based reaction depending on the reaction conditions. The Mn(III)-catalyzed aerobic oxidation of alkenes **1** in the presence of 4-hydroxyquinolin-2(1*H*)-ones **2** formed the bis(hydroperoxyethyl)quinolinones **3**, and the use of an excess amount of the Mn(III) catalyst in the case of 2-(1-arylvinyl)thiophene led to the azatrioxa[4.4.3]propellanes **4** and **5**. A similar reaction using 3-substituted quinolinones **6** afforded the endoperoxides **7** and/or hydroperoxides **8** depending on the bulkiness of the substituent at the 3-position of **6**. The oxidation of alkenes **1** with Mn(III)-quinolinone enolate complexes **A** at elevated temperature furnished the 3,5-dihydrofuro[3,2-*c*]quinolin-4-ones **9a**–**l** in high yields, and the reaction with conjugated butadienes **1′** proceeded in a 1,2-fashion to afford vinyl-substituted dihydrofuroquinolinones **9m**–**p**. The quinolinone analogues **11**, **13**, **15**, **17**, and **21** also produced the corresponding 2,3-dihydrofuro[3,2-*c*]pyridin-4-ones **12**, **14**, furo[3,2-*c*]pyran-4-ones **16**, **18**, benzofuran-4(5*H*)-ones **20**, and propellane **22** in moderate to high yields. The

Table 5
Mn(III)-mediated oxidation of 1,1-disubstituted ethenes **1** in the presence of 3-substituted quinolinones **6**[a]

Entry	Alkene **1**	Quinolinone **6**	Molar ratio of **1**/**6**/$Mn(OAc)_3 \cdot 2H_2O$	Temperature/°C	Time/min	Product (yield/%)[b]	
	Ph	Ar					
1	Ph	Me	1:2:3	Reflux	1.5	**23a** (56)	**24a** (25)[c]
2	Ph	Me	1:2:3	Reflux	2.5	**23a** (48)	**24a** (37)[c]
3	Ph	Me	1:2:3	Reflux	30		**24a** (79)
4	Ph	Me	1:2:3	80	24 h		**24a** (97)
5	Ph	Me	1:2:2:2[d]	23	3.5 h	**23a** (72)	**24a** (Trace)[c]
6	Ph	Pr	1:2:3	Reflux	2	**23b** (51)	**24b** (32)[c]
7	Ph	Bu	1:2:3	Reflux	6	**23c** (36)	**24c** (27)[c]
8	4-Cl-C_6H_4	Bu	1:2:3	Reflux	30	**23c** (Trace)	**24c** (78)[c]
9	4-Me-C_6H_4	Me	1:2:3	Reflux	2	**23d** (35)	**24d** (37)[c]
10	Ph	Me	1:2:3	Reflux	0.5		**24e** (55)

[a] The reaction was carried out under heated conditions in air except for entry 5.
[b] The yield was based on the amount of the alkene **1** used.
[c] The yield was calculated by crude NMR analysis.
[d] $Cu(OAc)_2$ was added as a co-oxidant and the reaction was conducted under an argon atmosphere.



Scheme 7. Oxidation pathway for the formation of **23** and **24**.

hemiacetals **23** and vinylquinolinones **24** could be synthesized depending on the reaction conditions. The new quinolinone derivatives and the related compounds obtained in the reactions will be screened for their biological activities such as antimalarial, insecticidal, bactericidal, cytotoxic, and antifeeding activities.

4. Experimental section

4.1. Measurements

Melting points were taken using a micromelting point apparatus and are uncorrected. The NMR spectra were recorded at 300 or 500 MHz for ^1H and 75 or 125 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm) and the coupling constants in hertz (Hz). The IR spectra were measured in $CHCl_3$ or KBr and expressed in cm^{-1}. The EIMS spectra were obtained by a gas chromatograph/mass spectrometer at an ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

4.2. 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 modified method described in the literature.[18,19] 4-Hydroxy-2-quinolinones **2**, **6**, 4-hydroxy-5,6,7,8-tetrahydroquinolin-2(1*H*)-one (**11**),[20] and 1-benzyl-4-hydroxy-5,6-dihydropyridin-2(1*H*)-one (**13**)[4a] were also prepared according to the methods reported in the literature. The 1,1-disubstituted alkenes **1** were prepared by the Grignard reaction of the corresponding acetophenones with arylmagnesium bromides followed by dehydration. 4-Hydroxy-2*H*-chromen-2-one (**15**), 4-hydroxy-6-methyl-2*H*-pyran-2-one (**17**), and dimedone (**19**) were purchased from Tokyo Kasei Co., Ltd., and Wako Pure Chemical Ind., Ltd., respectively, and used as received. The 2-(2-oxoethenyl)cyclohexane-1,3-dione **21** was prepared by the reaction of dimedone (**19**) with α-bromoacetophenone.

4.3. Mn(III)-catalyzed aerobic oxidation of a mixture of alkenes 2 and 4-hydroxyquinolin-2(1*H*)-ones

To a mixture of 1,1-diphenylethene **1** (Ar^1=Ar^2=Ph) (179.0 mg; 1 mmol) and quinolinone **2** (R=Me) (362.7 mg; 2.1 mmol) in glacial acetic acid (25 mL), $Mn(OAc)_3 \cdot 2H_2O$ (131.9 mg; 0.53 mmol) was added. The mixture was stirred at 23 °C in air for 4 h, and then the reaction was quenched by adding water (40 mL) to the reaction mixture. The aqueous solution was extracted five times with CH_2Cl_2 (10 mL×5) and the combined extracts were washed twice with water, a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and concentrated to dryness. The residue was separated by silica gel flash column chromatography eluting with CH_2Cl_2/hexane (7:3 v/v), giving bis(hydroperoxide) **3a** (210.1 mg; 71% yield based on the alkene **1** used) (Table 1, entry 6). Molar ratio and reaction times of other aerobic oxidation are shown in Tables 1 and 2. The products **3**–**5**, **7**, and **8** were further purified by recrystallization from an appropriate solvent for the analytical sample, and their physical data are given below.

*4.3.1. 3,3-Bis(2-hydroperoxy-2,2-diphenylethyl)-1-methylquinoline-2,4(1H,3H)-dione (**3a**: R=Me, Ar^1=Ar^2=Ph).* Colorless microcrystals (from MeOH), mp 134–135 °C. IR (KBr): ν 3400–3050 (OOH), 1668, 1624 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.14 (2H, s, OO*H*), 7.52–7.46 (1H, m, arom *H*), 7.24–7.10 (11H, m, arom *H*), 6.97–6.80 (12H, m, arom *H*), 3.66 (4H, s, CH_2×2), 3.00 (3H, s, NMe) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.3, 174.5 (*C*=O), 142.8 (2C, arom *C*), 142.5 (arom *C*), 141.8 (2C, arom *C*), 136.1 (C-7), 127.7 (8C, arom *CH*), 127.5 (C-5), 127.3 (8C, arom *CH*), 126.5 (2C, arom *CH*), 126.3 (2C, arom *CH*), 122.8 (C-6), 121.2 (arom *C*), 114.2 (C-8), 86.6 (2C, *C*OOH×2), 53.8 (C-3), 49.1 (2C, CH_2×2), 29.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{32}NO_4$ 566.2331 (M−OOH); found 566.2332.

*4.3.2. 3,3-Bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-1-methylquinoline-2,4(1H,3H)-dione (**3b**: R=Me, Ar^1=Ar^2=4-Cl-C_6H_4).* Colorless microcrystals (from CH_2Cl_2/hexane), mp 215–216 °C. IR (KBr): ν 3440–3100 (OOH), 1670,1629 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.20 (2H, s, OO*H*), 7.63–7.58 (1H, m, arom *H*), 7.29–7.01 (10H, m, arom *H*), 6.91–6.76 (9H, m, arom *H*),

3.60 (2H, d, *J*=14.1 Hz, *H*CH), 3.54 (2H, d, *J*=14.1 Hz, HC*H*), 3.16 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.5, 174.6 (*C*=O), 142.0 (2C, arom *C*), 141.0 (3C, arom *C*), 139.3 (2C, arom *C*), 136.8 (C-7), 133.6 (4C, arom *C*), 128.1 (8C, arom *C*H), 127.9 (C-5), 127.8 (4C, arom *C*H), 127.6 (4C, arom *C*H), 123.0 (C-6), 120.9 (arom *C*), 114.2 (C-8), 85.9 (2C, *C*OOH×2), 53.7 (C-3), 48.6 (CH_2×2), 29.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{30}Cl_4NO_6$ 736.0827 (M+H); found 736.0839. CCDC reference number, CCDC 217001.

*4.3.3. 3,3-Bis[2-hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-1-methylquinoline-2,4(1H,3H)-dione (**3c**: R=Me, Ar^1=Ar^2=4-Me-C$_6$H$_4$).* Pale yellow microcrystals (from MeOH), mp 134–136 °C. IR (KBr): ν 3300–3000 (OOH), 1668, 1600 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.15 (2H, s, OO*H*), 7.51–7.46 (1H, m, arom *H*), 7.13–6.96 (10H, m, arom *H*), 6.88–6.77 (5H, m, arom *H*), 6.61–6.58 (4H, m, arom *H*), 3.61 (4H, s, CH_2×2), 3.08 (3H, s, NCH_3), 2.28 (6H, s, Me×2), 2.04 (6H, s, Me×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.7, 174.8 (*C*=O), 142.4 (2C, arom *C*), 140.3 (1C, arom *C*), 138.6 (2C, arom *C*), 136.7 (2C, arom *C*), 136.5 (2C, arom *C*), 135.8 (C-7), 128.4 (8C, arom *C*), 127.8 (6C, arom *C*), 127.0 (C-5), 126.4 (C-4), 126.1, 121.7 (2C, arom *C*), 121.0 (arom *C*), 114.0 (C-8), 86.4 (2C, *C*OOH×2), 53.7 (C-3), 49.2 (CH_2×2), 29.7 (Me), 20.9 (Me×2), 20.6 (Me×2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{42}H_{40}NO_4$ 622.2957 (M−OOH); found 622.2924.

*4.3.4. 1-Ethyl-3,3-bis(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**3d**: R=Et, Ar^1=Ar^2=Ph).* Yellow microcrystals (from MeOH), mp 138–140 °C. IR (KBr): ν 3300–3057(OOH), 1666, 1608 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (2H, s, OO*H*), 7.47–7.41 (1H, m, arom *H*), 7.34–7.09 (13H, m, arom *H*), 6.94–6.71 (10H, m, arom *H*), 3.79 (2H, q, *J*=6.7 Hz, CH_2), 3.66 (4H, s, CH_2×2), 0.88 (3H, t, *J*=6.7 Hz, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6, 175.4 (*C*=O), 143.7 (2C, arom *C*), 141.1 (2C, arom *C*), 140.9 (arom *C*), 135.7 (C-7), 128.2 (2C, arom *C*), 128.1 (2C, arom *C*), 127.9 (4C, arom *C*), 127.7 (C-5), 127.6, 127.3, 127.1 (3C, arom *C*), 127.0 (4C, arom *C*), 126.5 (arom *C*), 126.3 (4C, arom *C*), 122.6 (C-6), 121.4 (arom *C*), 113.9 (C-8), 86.7 (2C, *C*OOH×2), 53.7 (C-3), 49.4 (2C, CH_2×2), 38.3 (CH_2), 11.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{39}H_{34}NO_4$ 580.2488 (M−OOH); found 580.2499.

*4.3.5. 1-Benzyl-3,3-bis(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**3e**: R=Bn, Ar^1=Ar^2=Ph).* Yellow microcrystals (from MeOH), mp 105–110 °C. IR (KBr): ν 3400–3026 (OOH), 1650, 1638 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40 (2H, s, OO*H*), 7.98–6.57 (29H, m, arom *H*), 5.04 (2H, s, CH_2), 3.74 (4H, s, CH_2×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 177.3 (*C*=O), 143.9 (3C, arom *C*), 141.4, 140.7(2C, arom *C*), 135.9 (arom *C*), 135.3 (C-7), 129.1 (C-5), 128.1 (6C, arom *C*H), 128.1 (arom *C*H), 127.7 (2C, arom *C*H), 127.3 (arom *C*H), 127.1 (2C, arom *C*H), 127.0 (6C, arom *C*H), 126.8 (2C, arom *C*H), 126.5 (2C, arom *C*H), 126.2 (3C, arom *C*H), 122.7 (C-6), 121.2 (arom *C*), 115.2 (C-8), 86.7 (2C, *C*OOH×2), 54.0 (CH_2), 49.6 (C-3), 49.1 (CH_2×2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{38}NO_6$ 676.2699 (M+H); found 676.2701.

*4.3.6. 1-Benzyl-3,3-bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl] quinoline-2,4(1H,3H)-dione (**3f**: R=Bn, Ar^1=Ar^2=4-Cl-C$_6$H$_4$).* Yellow microcrystals (from MeOH), mp 115–118 °C. IR (KBr): ν 3400–3060 (OOH), 1662, 1597 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.43 (2H, s, OO*H*), 7.88–6.59 (25H, m, arom *H*), 5.11 (2H, s, CH_2), 3.68 (2H, d, *J*=13.6 Hz, *H*CH), 3.59 (2H, d, *J*=13.6 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 177.1 (*C*=O), 141.8 (4C, arom *C*), 141.2, 138.3 (2C, arom *C*), 136.1 (C-7), 135.5 (arom *C*), 133.7 (2C, arom *C*), 133.5 (2C, arom *C*), 131.3 (2C, arom *C*H), 129.2 (C-5), 128.7 (2C, arom *C*H), 128.4 (4C, arom *C*H), 128.2 (arom *C*H), 128.0 (2C, arom *C*H), 127.7 (4C, arom *C*H), 127.2 (4C, arom *C*H), 127.0 (2C, arom *C*H), 122.9 (C-6), 115.2 (C-8), 86.1 (2C, *C*OOH×2), 53.9 (CH_2), 49.2 (C-3), 49.0 (CH_2×2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{44}H_{34}Cl_4NO_6$ 812.1140 (M+H); found 812.1149.

*4.3.7. 1-Benzyl-3,3-bis[2-hydroperoxy-2,2-bis(4-methylphenyl)ethyl] quinoline-2,4(1H,3H)-dione (**3g**: R=Bn, Ar^1=Ar^2=4-Me-C$_6$H$_4$).* Pale yellow microcrystals (from MeOH), mp 58–60 °C. IR (KBr): ν 3400–3000 (OOH), 1665, 1654 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.39 (2H, s, OO*H*), 7.71–6.39 (25H, m, arom *H*), 5.10 (2H, s, CH_2Ph), 3.70 (4H, s, CH_2×2), 2.28 (6H, s, Me×2), 1.95 (6H, s, Me×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 177.6 (*C*=O), 141.6 (arom *C*), 141.2 (2C, arom *C*), 137.6 (2C, arom *C*), 136.8 (2C, arom *C*), 136.4 (2C, arom *C*), 136.0 (arom *C*), 135.1 (C-7), 130.2 (arom *C*H), 129.1 (2C, arom *C*H), 128.8 (2C, arom *C*H), 128.7 (4C, arom *C*H), 127.7 (C-6), 127.5 (4C, arom *C*H), 126.9 (2C, arom *C*H), 126.1 (arom *C*), 126.6 (2C, arom *C*H), 126.2 (4C, arom *C*), 121.4 (C-5), 115.2 (C-8), 86.6 (2C, *C*OOH×2), 54.0 (C-3), 49.6 (2C, CH_2×2), 49.3 (CH_2), 20.9 (2C, Me×2), 20.5 (2C, Me×2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{48}H_{44}NO_4$ 698.3270 (M−OOH); found 698.3268.

*4.3.8. 3,4-Dihydro-10-methyl-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4a**: R=Me, Ar^1=Ar^2=Ph).* Colorless microcrystals (from CH_2Cl_2/hexane), mp 134–135 °C. IR (KBr): ν 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82–7.79 (2H, m, arom *H*), 7.58–6.92 (21H, m, arom *H*), 6.77–6.72 (1H, m, arom *H*), 3.33 (3H, s, Me), 3.25 (1H, d, *J*=12.9 Hz, *H*CH), 3.10 (1H, d, *J*=14.4 Hz, *H*CH), 2.80 (1H, d, *J*=12.9 Hz, HC*H*), 2.54 (1H, d, *J*=14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.7 (*C*=O), 148.2, 145.2, 143.9, 142.5, 142.4 (arom *C*), 136.3, 132.4, 130.1, 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.8 (2C), 127.6 (2C), 127.3, 127.1, 126.9, 126.6 (2C), 126.4 (2C), 126.0 (2C), 118.4, 113.4 (arom *C*H), 117.1, 114.6 (C-5a and C-10a), 87.1 (C-3), 84.3 (C-12), 53.4 (C-4a), 43.2 (CH_2), 38.3 (CH_2), 30.3 (Me) ppm. Anal. Calcd for $C_{38}H_{31}NO_4 \cdot 1/4H_2O$: C, 80.05; H,5.57; N, 2.46. Found: C, 80.13; H, 5.63; N, 2.52. CCDC reference number, CCDC 218561.

*4.3.9. 3,3,12,12-Tetrakis(4-chlorophenyl)-3,4-dihydro-10-methyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4b**: R=Me, Ar^1=Ar^2=4-Cl-C$_6$H$_4$).* Yellow microcrystals (from MeOH), mp 115–116 °C. IR (KBr): ν 1651 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–6.75 (20H, m, arom *H*), 3.33 (3H, s, Me), 3.27 (1H, d, *J*=12.2 Hz, *H*CH), 3.10 (1H, d, *J*=14.0 Hz, *H*CH), 2.80 (1H, d, *J*=12.2 Hz, HC*H*), 2.54 (1H, d, *J*=14.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6 (*C*=O), 148.2 (2C), 145.2 (2C), 143.9 (2C), 142.4 (2C, arom *C*), 136.3, 128.4 (2C), 128.3 (2C), 127.9, 127.7 (2C), 127.5 (2C), 126.9, 126.6 (2C), 126.4 (2C), 126.0 (4C), 118.4, 113.4 (arom *C*H), 117.1, 114.6 (C-5a and C-10a), 87.1 (C-3), 84.3 (C-12), 53.5 (C-4a), 43.2, 38.4 (CH_2), 30.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{38}H_{28}Cl_4NO_4$ 702.0772 (M+H); found 702.0768.

*4.3.10. 3,4-Dihydro-3,3,12,12-tetrakis(4-methylphenyl)-10-methyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4c**: R=Me, Ar^1=Ar^2=4-Me-C$_6$H$_4$).* . Pale yellow microcrystals (from MeOH), mp 174–175 °C. IR (KBr): ν 1672 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–6.64 (20H, m, arom *H*), 3.29(3H, s, Me), 3.17 (1H, d, *J*=13.0 Hz, *H*CH), 3.04 (1H, d, *J*=11.0 Hz, *H*CH), 2.83 (1H, d, *J*=13.0 Hz, HC*H*), 2.48 (1H, d, *J*=11.0 Hz, HC*H*), 2.37 (3H, s, Me), 2.26 (3H, s, Me), 2.20 (3H, s, Me), 2.17 (3H, s, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9 (*C*=O), 148.3, 136.8 (2C), 136.6 (2C), 136.2 (2C), 136.1 (2C, arom *C*), 136.6, 130.2, 129.3 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 128.4 (2C), 128.2 (2C), 126.6 (2C), 125.4 (2C), 118.2, 113.3 (arom *C*H), 117.0, 114.5 (C-5a and C-10a), 92.0 (C-3), 87.0 (C-12), 51.0 (C-4a), 39.1, 38.4 (CH_2), 30.3 (Me), 21.0 (Me), 20.9

(Me×3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{42}H_{40}NO_4$ 622.2957 (M+H); found 622.2958.

*4.3.11. 10-Ethyl-3,4-dihydro-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4d**: R=Et, Ar^1=Ar^2=Ph).* Yellow microcrystals (from MeOH), mp 159–161 °C. IR (KBr): ν 1674 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82–7.79 (1H, m, arom *H*), 7.61–7.57 (4H, m, arom *H*), 7.51–7.45 (4H, m, arom *H*), 7.37–7.28 (4H, m, arom *H*), 7.19–7.00 (8H, m, arom *H*), 6.89–6.85 (2H, m, arom *H*), 6.75–6.70 (1H, m, arom *H*), 4.09–3.83 (2H, m, CH_2), 3.24 (1H, d, *J*=12.5 Hz, *H*CH), 3.10 (1H, d, *J*=14.5 Hz, *H*CH), 2.78 (1H, d, *J*=12.5 Hz, HC*H*), 2.46 (1H, d, *J*=14.5 Hz, HC*H*), 1.49 (3H, t, *J*=7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6 (*C*=O), 147.3, 145.5, 144.2, 142.8, 142.2 (arom *C*), 136.2, 132.4, 130.1, 128.7, 128.4 (2C), 128.3 (2C), 127.9, 127.7 (2C), 127.6 (2C), 126.9, 126.6 (2C), 126.2 (2C), 125.9 (2C), 125.8 (2C), 118.0, 113.5 (arom *C*H), 117.0, 114.9 (C-5a and C-10a), 87.0 (C-3), 84.2 (C-12), 53.6 (C-4a), 42.6, 38.6, 38.2 (*C*H_2), 13.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{39}H_{34}NO_4$ 580.2488 (M+H); found 580.2487.

*4.3.12. 3,4-Dihydro-3,3,12,12-tetraphenyl-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4h**: R=H, Ar^1=Ar^2=Ph).* Yellow microcrystals (from MeOH), mp 190–192 °C. IR (KBr): ν 3200–2940 (NH), 1660 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82–7.79 (2H, m, arom *H*), 7.57–7.44 (5H, m, arom *H*), 7.35–6.91 (15H, m, arom *H*), 6.75–6.70 (2H, m, arom *H*), 5.76 (1H, s, N*H*), 3.25 (1H, d, *J*=13.2 Hz, *H*CH), 3.15 (1H, d, *J*=14.4 Hz, *H*CH), 2.84 (1H, d, *J*=13.2 Hz, HC*H*), 2.57 (1H, d, *J*=14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9 (*C*=O), 146.3, 145.1, 142.4, 142.1, 137.6 (arom *C*), 135.9, 132.4, 130.1 (2C), 128.4, 128.3 (2C), 128.2 (2C), 128.0, 127.8 (2C), 127.6, 126.9, 126.6 (2C), 126.3 (2C), 126.0 (2C), 125.9 (2C), 119.5, 115.9 (arom *C*H), 116.3, 112.7 (C-5a and C-10a), 87.5 (C-3), 84.4 (C-12), 53.2 (C-4a), 43.0, 37.9 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{37}H_{30}NO_4$ 552.2175 (M+H); found 552.2092.

*4.3.13. 3,4-Dihydro-10-methyl-3,12-diphenyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4i**: R=Me, Ar^1=Ph, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Colorless needles (from EtOAc/hexane), mp 185–187 °C (decomp.). IR ($CHCl_3$): ν 1672 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78–6.76 (20H, m, arom *H*), 3.40 (1H, d, *J*=13.0 Hz, *H*CH), 3.33 (3H, s, Me), 3.05 (1H, d, *J*=15.0 Hz, *H*CH), 2.90 (1H, d, *J*=13.0 Hz, HC*H*), 2.52 (1H, d, *J*=15.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9 (*C*=O), 150.2, 147.3, 145.4, 143.4, 141.8 (arom *C*), 136.4, 128.2 (2C), 128.0 (2C), 127.7, 127.4 (2C), 126.7, 126.6, 126.3, 126.2 (2C), 126.1, 125.9, 125.8 (2C), 125.7, 118.6, 113.4 (arom *C*H), 117.0, 114.7 (C-5a and C-10a), 84.7 (C-3), 83.0 (C-12), 53.3 (C-4a), 45.3, 39.6 (*C*H_2), 30.3 (Me) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{34}H_{27}NO_4S_2Na$ 600.1279 (M+Na); found 600.1284.

*4.3.14. 3,12-Bis(4-fluorophenyl)-3,4-dihydro-10-methyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one(**4j**: R=Me, Ar^1=4-F-C_6H_4, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Amorphous. IR ($CHCl_3$): ν 1670 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.72–6.74 (18H, m, arom *H*), 3.33 (3H, s, Me), 3.08 (1H, d, *J*=15.0 Hz, *H*CH), 2.98 (1H, d, *J*=12.6 Hz, *H*CH), 2.80 (1H, d, *J*=12.6 Hz, HC*H*), 2.58 (1H, d, *J*=15.0 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9 (*C*=O), 160.8, 160.3, 149.6, 148.1, 146.8, 141.4, 138.9 (arom *C*), 136.7, 136.5, 128.7, 128.6, 128.4 (2C), 127.7 (2C), 127.1, 126.7, 126.4 (2C), 126.3 (4C), 118.8, 113.6 (arom *C*H), 116.9, 114.7 (C-5a and C-10a), 84.4 (C-3), 82.9 (C-12), 53.6 (C-4a), 44.5, 39.4 (*C*H_2), 30.3 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{34}H_{26}F_2NO_4S_2$ 614.1271 (M+H); found 614.1269.

*4.3.15. 3,4-Dihydro-3,12-bis(4-methylphenyl)-10-methyl-3,12-bis(2-thienyl)-10a,4a-(epoxyethano)-1,2-dioxino[3,4-b]quinolin-5(10H)-one (**4k**: R=Me, Ar^1=4-Me-C_6H_4, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Amorphous. IR ($CHCl_3$): ν 1670 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76–6.71 (18H, m, arom *H*), 3.30 (3H, s, Me), 3.26 (1H, d, *J*=12.9 Hz, *H*CH), 3.06 (1H, d, *J*=15.0 Hz, *H*CH), 2.90 (1H, d, *J*=12.9 Hz, HC*H*), 2.56 (1H, d, *J*=15.0 Hz, HC*H*), 2.29 (3H, s, Me), 2.19 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.1 (*C*=O), 147.5, 138.1, 137.4, 136.9, 136.5, 136.4, 136.4 (arom *C*), 136.3, 129.2, 128.9, 128.4, 128.2, 128.1, 126.7 (2C), 126.0 (2C), 125.9 (2C), 125.7 (2C), 125.5 (2C), 118.4, 113.5 (arom CH), 117.0, 114.7 (C-5a and C-10a), 84.6 (C-3), 82.9 (C-12), 53.7 (C-4a), 45.0, 39.6 (*C*H_2), 30.3 (N–*C*H_3), 21.0, 20.9 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{36}H_{32}NO_4S_2$ 606.1773 (M+H); found 606.1782.

*4.3.16. 3,4-Dihydro-6-methyl-3,12-diphenyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5i**: R=Me, Ar^1=Ph, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Colorless needles (from EtOAc/hexane), mp 244–246 °C (decomp.). IR ($CHCl_3$): ν 1662 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.02–7.92 (1H, m, arom *H*), 7.49–6.70 (19H, m, arom *H*), 3.07 (3H, s, Me), 3.23 (1H, d, *J*=14.7 Hz, *H*CH), 3.18 (1H, d, *J*=15.0 Hz, *H*CH), 2.90 (1H, d, *J*=15.0 Hz, HC*H*), 2.33 (1H, d, *J*=14.7 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2 (*C*=O), 149.7, 148.7, 147.2, 146.9, 144.8, 143.3, 130.7, 130.6, 128.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.3, 126.7, 126.5, 126.4, 126.3, 126.2, 126.0, 125.9, 125.8, 125.5, 125.4, 125.3, 125.1, 124.9, 123.6, 123.5, 120.7, 120.5, 114.4, 106.8 (C-10b), 86.9 (C-3), 83.5 (C-12), 51.5 (C-4a), 46.2 (C-4), 40.2 (C-13), 29.8 (N–*C*H_3) ppm. FAB HRMS (acetone/NBA/NaI): calcd for $C_{34}H_{27}NO_4S_2Na$ 600.1279 (M+Na); found 600.1357.

*4.3.17. 3,12-Bis(4-fluorophenyl)-3,4-dihydro-6-methyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5j**: R=Me, Ar^1=4-F-C_6H_4, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Colorless needles (from EtOAc/hexane), mp 172–173 °C. IR ($CHCl_3$): ν 1668 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.00–6.44 (18H, m, arom *H*), 3.45 (2H, s, CH_2), 3.18 (1H, d, *J*=14.4 Hz, *H*CH), 2.95 (3H, s, Me), 2.30 (1H, d, *J*=14.4 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0 (*C*=O), 163.7, 160.3, 149.4, 146.8, 139.2 (arom *C*), 130.8, 130.7, 128.7, 128.6, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.8, 126.5, 126.4, 126.3, 126.2, 126.0, 123.8 (arom *C*H), 120.5 (arom *C*), 115.6, 115.3, 115.2, 114.9, 114.5, 114.4, 114.1 (arom *C*H), 106.5 (C-10b), 86.5 (C-3), 83.2 (C-12), 51.7 (C-4a), 46.2 (C-4), 40.2 (C-13), 29.8 (N–*C*H_3) ppm. FAB HRMS (acetone/NBA): calcd for $C_{34}H_{26}F_2NO_4S_2$ 614.1271 (M+H); found 614.1288.

*4.3.18. 3,4-Dihydro-3,12-bis(4-methylphenyl)-6-methyl-3,12-bis(2-thienyl)-10b,4a-(epoxyethano)-1,2-dioxino[4,3-c]quinolin-5(6H)-one (**5k**: R=Me, Ar^1=4-Me-C_6H_4, Ar^2=2-thienyl).* The diastereomixture could not be purified and the physical data of one of the diastereomers are shown as follows. Amorphous. IR ($CHCl_3$): ν1652 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.01–7.98 (1H, m, arom *H*), 7.67–6.94 (15H, m, arom *H*), 6.76–6.72 (1H, m, arom *H*), 6.53–6.47 (1H, m, arom *H*), 3.45 (2H, s, CH_2), 3.20 (1H, d, *J*=15.0 Hz, *H*CH), 2.91 (3H, s, Me), 2.32 (1H, d, *J*=15.0 Hz, HC*H*), 2.27 (3H, s, Me), 2.20 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3 (*C*=O), 149.9, 140.5, 137.7, 137.0 (arom *C*), 130.6, 129.2, 128.9, 128.1, 127.9, 126.6, 126.4, 126.3, 126.2, 126.1, 125.9, 125.8, 125.7, 125.2, 123.6,

120.8, 114.4 (arom *C*H), 106.5 (C-10b), 86.9 (C-3), 83.4 (C-12), 51.5 (C-4a), 46.1 (C-4), 40.2 (C-13), 29.8 (N–*C*H$_3$), 21.1 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{36}H_{31}NO_4S_2$ 606.1773 (M+H); found 606.1765.

*4.3.19. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7a**: R=Me, Ar=Ph).* Colorless microcrystals (from CH_2Cl_2/hexane), mp 195 °C (decomp.). IR (KBr): *ν* 3382–2929 (OH and NH), 1678 (*C*=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.1 (1H, s, N*H*), 7.73–7.70 (1H, m, arom *H*), 7.57 (1H, br s, arom *H*), 7.46–7.43 (3H, m, arom *H*), 7.34–7.01 (8H, m, arom *H*), 6.77–6.75 (1H, m, arom *H*), 3.47 (1H, br s, O*H*), 3.34 (1H, br, *H*CH), 2.75 (1H, d, *J*=13.5 Hz, HC*H*), 1.10 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 171.2 (*C*=O), 144.8, 142.0 (2C, arom *C*), 136.7 (2C, arom *C*), 130.4 (arom *C*), 128.0 (4C, arom *C*H), 127.2 (2C, arom *C*H), 127.1 (arom *C*), 127.0 (2C, arom *C*H), 126.3 (arom *C*H), 125.4 (2C, arom *C*H), 122.0 (arom *C*H), 99.0 (C-10b), 84.4 (C-3), 44.0 (C-4a), 30.3 (*C*H$_2$), 22.3 (Me) ppm. Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.20; H, 5.41; N, 3.59.

*4.3.20. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-4a-propyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7b**: R=Pr, Ar=Ph).* Colorless microcrystals (from MeOH), mp 145–147 °C. IR (KBr): *ν* 3392–2873 (OH and NH), 1662 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): *δ* 10.02 (1H, s, NH), 7.70–7.66 (1H, m, arom *H*), 7.49–7.40 (2H, m, arom *H*), 7.32–6.98 (10H, m, arom *H*), 6.70–6.68 (1H, m, arom *H*), 3.79 (1H, d, *J*=13.1 Hz, *H*CH), 2.59 (1H, d, *J*=13.1 Hz, HC*H*), 2.50 (1H, s, O*H*), 1.52 (2H, t, *J*=5.8 Hz, C*H*$_2$), 1.09–0.91 (2H, m, C*H*$_2$), 0.68 (3H, t, *J*=7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): *δ* 169.8 (*C*=O), 145.4, 142.0, 136.9 (arom *C*), 130.6, 128.1, 127.3, 127.0, 126.7, 125.4, 122.0 (arom *C*H), 121.1 (arom *C*), 114.3 (arom *C*H), 98.7 (C-10b), 84.4 (C-3), 47.4 (C-4a), 39.4, 34.6, 16.5 (*C*H$_2$), 14.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{26}NO_4$ 416.1862 (M+H); found 416.1862.

*4.3.21. 4a-Butyl-4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-diphenyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7c**: R=Bu, Ar=Ph).* The product **7c** could not be separated from **8c** by silica gel chromatography. Yellow microcrystals (from CH_2Cl_2/hexane), mp148–152 °C. IR (KBr): *ν* 3600–2900 (OH and NH), 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.05 (1H, s, N*H*), 7.81–6.61 (14H, m, arom *H*), 5.43 (1H, s, O*H*), 3.81 (1H, d, *J*=14.1 Hz, *H*CH), 2.73 (1H, d, *J*=14.1 Hz, HC*H*), 2.13 (2H, m, C*H*$_2$), 1.34–1.16 (4H, m, C*H*$_2$×2), 0.74 (3H, t, *J*=6.9 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 171.6 (*C*=O), 143.5, 141.9, 140.3 (arom *C*), 135.9, 128.5, 127.8, 127.6, 127.4, 126.6, 123.3, 115.0 (arom *C*H), 99.5 (C-10b), 86.0 (C-3), 48.3 (C-4a), 36.7, 35.2, 25.3, 23.1 (*C*H$_2$), 13.8 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{27}H_{28}NO_4$ 430.2018 (M+H); found 430.2021.

*4.3.22. 4,4a,6,10b-Tetrahydro-10b-hydroxy-4a,3,3-triphenyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7d**: R=Ar=Ph).* The product **7d** could not be separated from **8d** by silica gel chromatography. Colorless microcrystals (from MeOH), mp 151 °C. IR (KBr): *ν* 3400–2940 (OH and NH), 1697, 1659 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.32 (1H, s, N*H*), 7.52–7.01 (17H, m, arom *H*), 6.83–6.80 (1H, m, arom *H*), 6.44–6.41 (1H, m, arom *H*), 5.27 (O*H*), 4.16 (1H, d, *J*=14.1 Hz, *H*CH), 3.25 (1H, d, *J*=14.1 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.4 (*C*=O), 143.4, 142.2, 140.3, 139.8 (arom *C*), 131.2, 129.1, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 126.1, 123.7, 123.5, 116.5 (arom *C*H), 118.7 (arom *C*), 99.0 (C-10b), 86.0 (C-3), 52.4 (C-4a), 36.4 (*C*H$_2$) ppm. FAB HRMS (acetone/NBA): calcd for $C_{29}H_{24}NO_4$ 450.1705 (M+H); found 450.1650.

*4.3.23. 3,3-Bis(4-chlorophenyl)-4,4a,6,10b-tetrahydro-10b-hydroxy-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7e**: R=Me, Ar=4-Cl-C$_6$H$_4$).* Pale yellow microcrystals (from MeOH), mp 155–157 °C. IR (KBr): *ν* 3400–3060 (OH), 3300–2900 (NH), 1678 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.0 (1H, s, N*H*), 7.85–7.76 (1H, m, arom *H*), 7.49–6.89 (10H, m, arom *H*), 6.79–6.77 (1H, m, arom *H*), 5.45 (1H, s, O*H*), 3.54 (1H, d, *J*=13.1 Hz, *H*CH), 2.78 (1H, d, *J*=13.1 Hz, HC*H*), 1.15 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 170.2 (*C*=O), 141.6 (arom *C*), 139.0 (2C, arom *C*), 135.6 (arom *C*), 130.5 (2C, arom *C*), 129.3 (2C, arom *C*H), 128.0 (C-5), 126.9 (2C, arom *C*H), 126.2 (2C, arom *C*H), 126.1 (arom *C*H), 125.8 (2C, arom *C*H), 122.3 (arom *C*H), 114.8 (arom *C*H), 98.0 (C-10b), 83.1 (C-3), 52.6 (C-4a), 43.0 (*C*H$_2$), 21.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}Cl_2NO_4$ 456.0769 (M+H); found 456.0779.

*4.3.24. 4,4a,6,10b-Tetrahydro-10b-hydroxy-3,3-bis(4-methylphenyl)-4a-methyl-1,2-dioxino[4,3-c]quinolin-5(3H)-one (**7f**: R=Me, Ar=4-Me-C$_6$H$_4$).* The product **7f** could not be separated from **8f** by silica gel chromatography. Orange microcrystals (from MeOH), mp 192–193 °C; IR (KBr): *ν* 3400–2877 (OH and NH), 1683 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.2 (1H, s, N*H*), 7.54–6.64 (12H, m, arom *H*), 5.22 (1H, s, O*H*), 3.84 (1H, d, *J*=14.4 Hz, *H*CH), 2.75 (1H, d, *J*=14.4 Hz, HC*H*), 2.15, 2.11 (6H, s, Me×2), 1.53 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 173.2 (*C*=O), 141.2, 140.9, 138.2, 137.8, 136.1, 136.0 (arom *C*), 129.9, 129.0, 128.9, 128.1, 128.0, 127.4, 127.3, 126.9, 126.2, 126.6, 124.8, 122.9 (arom *C*H), 99.5 (C-10b), 86.0 (C-3), 52.4 (C-4a), 45.4 (*C*H$_2$), 20.8 (Me), 20.7 (Me), 8.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M–OOH); found 382.1847.

*4.3.25. 3-(2-Hydroperoxy-2,2-diphenylethyl)-3-propylquinoline-2,4(1H,3H)-dione (**8b**: R=Pr, Ar=Ph).* The product **8b** could not be separated from **7b** by silica gel chromatography. Colorless microcrystals (from MeOH), mp 145–147 °C. IR (KBr): *ν* 3392–2873 (OOH and NH), 1680, 1662 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CHCl_3$): *δ* 9.68 (1H, s, N*H*), 9.33 (1H, s, OO*H*), 7.81–6.62 (14H, m, arom *H*), 3.58 (1H, d, *J*=14.7 Hz, *H*CH), 3.51 (1H, d, *J*=14.7 Hz, HC*H*), 2.12–2.08 (2H, t, *J*=5.2 Hz, C*H*$_2$), 1.23–0.96 (2H, m, C*H*$_2$), 0.792 (3H, t, *J*=7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CHCl_3$): *δ* 197.2, 176.9 (*C*=O), 143.5, 140.4, 136.2 (arom *C*), 127.5, 127.4, 127.0, 126.5, 126.3, 125.5, 120.1, 119.8 (arom *C*H), 86.0 (*C*OOH), 57.2 (C-3), 39.3, 36.0, 16.7 (*C*H$_2$), 14.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{26}NO_4$ 416.1862 (M+H); found 416.1862.

*4.3.26. 3-Butyl-3-(2-hydroperoxy-2,2-diphenylethyl)quinoline-2,4(1H,3H)-dione (**8c**: R=Bu, Ar=Ph).* The product **8c** could not be separated from **7c** by silica gel chromatography. Yellow microcrystals (from CH_2Cl_2/hexane), mp 148–152 °C. IR (KBr): *ν* 3500–2770 (OOH and NH), 1680, 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 9.65 (1H, s, N*H*), 9.17 (1H, s, OO*H*), 7.81–6.61 (14H, m, arom *H*), 3.59 (1H, d, *J*=14.7 Hz, *H*CH), 3.53 (1H, d, *J*=14.7 Hz, HC*H*), 1.78–1.16 (6H, m, CH$_2$×3), 0.74, (3H, t, *J*=7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 197.4, 176.9 (*C*=O), 143.5, 141.9, 140.9, 140.3 (arom *C*), 135.9, 128.5, 127.8, 127.6, 127.4, 127.3, 127.2, 126.6, 126.3, 125.7, 123.3, 116.3 (arom *C*H), 86.9 (*C*OOH), 57.0 (C-3), 45.5, 44.8, 25.3, 22.8 (*C*H$_2$×4), 13.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{27}H_{28}NO_4$ 430.2018 (M+H); found 430.2021.

*4.3.27. 3-(2-Hydroperoxy-2,2-diphenylethyl)-3-phenylquinoline-2,4(1H,3H)-dione (**8d**: R=Ar=Ph).* The product **8d** could not be separated from **7d** by silica gel chromatography. Colorless microcrystals (from CH_2Cl_2/hexane), mp 151 °C. IR (KBr): *ν* 3400–2940 (OOH and NH), 1697, 1659 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 9.87 (1H, s, N*H*), 9.02 (1H, s, OO*H*), 7.77–7.74 (1H, m, arom *H*), 7.65–7.63 (1H, m, arom *H*), 7.52–7.01 (17H, m, arom *H*), 4.10 (1H, d, *J*=14.1 Hz, *H*CH), 3.91 (1H, d, *J*=14.1 Hz, HC*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 194.3, 175.3 (*C*=O), 143.8, 141.0, 138.1, 135.7 (arom *C*), 129.1, 128.5, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 127.0,

126.9, 126.7, 126.6, 126.4, 126.1, 123.7, 123.5, 115.5 (arom *C*H), 120.5 (arom *C*), 87.2 (*C*OOH), 60.8 (C-3), 42.6 (*C*H_2). FAB HRMS (acetone/NBA): calcd for $C_{29}H_{24}NO_4$ 450.1705 (M+H); found 450.1650.

*4.3.28. 3-[2-Hydroperoxy-2,2-bis(4-methylphenylethyl)]-3-methylquinoline-2,4(1H,3H)-dione (**8f**: R=Me, Ar=4-Me-C_6H_4).* The product **8f** could not be separated from **7f** by silica gel chromatography. IR (KBr): ν 3400–2877 (OOH and NH), 1683 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.80 (1H, s, N*H*), 9.43 (1H, s, OO*H*), 7.83–6.67 (12H, m, arom *H*), 3.75 (1H, d, *J*=14.4 Hz, *H*CH), 3.70 (1H, d, *J*=14.47 Hz, HC*H*), 2.04 (3H, s, Me), 1.93 (3H, s, Me), 1.28 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 175.5 (*C*=O), 141.1, 141.0, 140.5, 137.0, 136.6, 136.5 (arom *C*), 135.9, 130.2, 129.1, 128.9, 128.7, 128.5, 128.3, 127.4, 123.5, 122.5 (arom *C*H), 84.0 (*C*OOH), 53.4 (C-3), 44.6 (*C*H_2), 22.1 (Me), 21.0 (Me), 16.2 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M−OOH); found 382.1847.

4.4. Approach to the interconversion between 3a and 4a

The bis(hydroperoxide) **3a** (R=Me, Ar^1=Ar^2=Ph) and the propellane **4a** (R=Me, Ar^1=Ar^2=Ph) (0.1 mmol), respectively, were stirred in glacial acetic acid (10 mL) at room temperature in the absence and the presence of $Mn(OAc)_3$ (0.1 mmol) for 4 h. After the usual work-up, the bis(hydroperoxide) **3a** and the propellane **4a** were recovered in 99% and 91%, respectively, in the absence of the oxidant, while **3a** in 48% and **4a** in 83% recoveries in the presence of $Mn(OAc)_3$. No isolable products were obtained from both reactions.

4.5. Mn(III)-mediated oxidation of alkenes in the presence of 4-hydroxyquinolin-2(1*H*)-ones and the related substrates at reflux temperature

A mixture of 1,1-diphenylethene **1** (Ar=Ph) (181.3 mg; 1 mmol), 4-hydroxy-2-quinolinone **2** (R=Me, X=H) (351.4 mg; 2 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (814.4 mg; 3 mmol) in glacial acetic acid (25 mL) was heated under reflux until the brown color of Mn(III) disappeared (normally for 3 min). The solvent was removed in vacuo and water (25 mL) was added to the reaction mixture. The aqueous solution was then extracted three times with dichloromethane (20 mL). The combined extracts were washed with a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated on silica gel TLC developed with 5% methanol/dichloromethane, giving the products **9a** (310.6 mg; 87%) and **10a** (23.6 mg; 7%) (Table 3, entry 2). Molar ratio and reaction times of other oxidation are shown in Tables 3–5. The products were further purified by recrystallization from an appropriate solvent for the analytical sample, and their physical data are given below.

*4.5.1. 3,5-Dihydro-5-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9a**: R=Me, X=H, Ar=Ph).*[10c] Yield 87% (Table 3, entry 2).

*4.5.2. 3,9-Dihydro-9-methyl-2,2-diphenylfuro[2,3-b]quinolin-4(2H)-one (**10a**: R=Me, Ar=Ph).*[10c] Yield 7% (Table 3, entry 2).

*4.5.3. 5-Ethyl-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9b**: R=Et, X=H, Ar=Ph).* Yield 73% (Table 3, entry 3). Colorless microcrystals (from MeOH), mp 181–182 °C. IR (KBr): ν 1666 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.01–7.99 (1H, m, arom *H*), 7.59–7.25 (13H, m, arom *H*), 4.35 (2H, q, *J*=7.0 Hz, CH_2), 3.97 (2H, s, CH_2), 1.33 (3H, t, *J*=7.0 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0, 160.6 (*C*=O and *C*=C), 144.5, 139.8 (arom *C*), 130.9, 128.3, 127.7, 125.8, 123.3, 121.4, 114.5 (arom *C*H), 112.8, 107.7 (arom *C*), 95.7 (C-2), 42.8, 36.9 (*C*H_2×2), 13.1 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{25}H_{22}NO_2$ 368.1651 (M+H); found 368.1688.

*4.5.4. 3,5-Dihydro-2,2-diphenyl5-propylfuro[3,2-c]quinolin-4(2H)-one (**9c**: R=Pr, X=H, Ar=Ph).* Yield 76% (Table 3, entry 4). Colorless needles (from MeOH), mp 161 °C. IR (KBr): ν 1662 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.07–7.98 (1H, m, arom *H*), 7.57–7.11 (13H, m, arom *H*), 4.23 (2H, m, CH_2), 3.97 (2H, s, CH_2), 1.76–1.55 (2H, m, $CH_2CH_2CH_3$), 1.03 (3H, t, *J*=7.3 Hz, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0, 160.9 (*C*=O and *C*=C), 144.6, 140.0 (arom *C*), 130.8, 128.4, 128.3, 127.7, 127.5, 125.8, 123.2, 114.6 (arom *C*H), 121.4, 112.7, 107.6 (arom *C*), 95.6 (C-2), 43.5, 42.8, 21.1 (*C*H_2), 11.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1834.

*4.5.5. 5-Benzyl-3,5-Dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9d**: R=Bn, X=H, Ar=Ph).* Yield 85% (Table 3, entry 5). Pale orange microcrystals (from MeOH), mp 221 °C. IR (KBr): ν 1656 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.99–7.97 (1H, m, arom *H*), 7.53–7.17 (18H, m, arom *H*), 5.52 (2H, br s, CH_2), 4.04 (2H, s, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5, 161.3 (*C*=O and *C*=C), 144.5, 140.2, 136.8 (arom *C*), 131.1, 128.7, 128.5, 127.9, 127.1, 126.5, 125.8, 123.2, 121.9, 115.6 (arom *C*H), 112.7, 107.4 (arom *C*), 95.9 (C-2), 45.6, 42.7 (*C*H_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{30}H_{24}NO_2$ 430.1807 (M+H); found 430.1815.

*4.5.6. 3,5-Dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9e**: R=X=H, Ar=Ph).* Yield 73% (Table 3, entry 6). Colorless microcrystals (from MeOH), mp 242 °C (decomp.). IR (KBr): ν 3200–2740 (N*H*), 1654 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 11.5 (1H, s, NH), 8.30–7.79 (2H, m, arom *H*), 7.64–7.22 (12H, m, arom *H*), 3.80 (2H, CH_2) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.1, 160.5 (*C*=O and *C*=C), 144.5, 139.7 (arom *C*), 131.0, 128.8, 1.28.5, 127.7, 127.2, 126.2, 125.3, 121.9, 121.7, 115.6 (arom *C*H), 110.6, 107.8 (arom *C*), 95.2 (C-2), 41.6 (*C*H_2) ppm. Anal. Calcd for $C_{23}H_{17}NO_2 \cdot 2H_2O$: C, 79.29; H, 5.21; N, 4.02. Found: C, 79.45; H, 4.87; N, 4.04.

*4.5.7. 2,2-Bis(4-chlorophenyl)-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9f**: R=Me, X=H, Ar=4-Cl-C_6H_4).* Yield 87% (Table 3, entry 7). Colorless microcrystals (from EtOH), mp 194–195 °C. IR (KBr): ν 1645 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94–7.92 (1H, m, arom *H*), 7.59–7.57 (1H, m, arom *H*), 7.41–7.25 (10H, m, arom H), 3.90 (2H, s, CH_2), 3.69 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.8, 160.7 (*C*=O and *C*=C), 142.5, 140.8, 134.0 (arom *C*), 131.2, 128.7, 127.3, 122.9, 121.8, 114.7 (arom *C*H), 112.3, 107.4 (arom *C*), 94.7 (C-2), 42.6 (*C*H_2), 29.1 (Me) ppm. Anal. Calcd for $C_{24}H_{17}Cl_2NO_2$: C, 68.26; H, 4.06; N, 3.32. Found: C, 68.29; H, 4.17; N, 3.59.

*4.5.8. 2,2-Bis(4-chlorophenyl)-3,9-dihydro-9-methylfuro[2,3-b]quinolin-4(2H)-one (**10f**: R=Me, X=H, Ar=4-Cl-C_6H_4).* Yield 12% (Table 3, entry 7). Colorless microcrystals (from MeOH), mp 124–125 °C. IR (KBr): ν 1589 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.43 (1H, d, *J*=7.8 Hz, arom H), 7.63–7.28 (11H, m, arom H), 3.95 (2H, s, CH_2), 3.82 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7 (*C*=O), 159.5 (*C*=C), 141.5, 138.6, 134.3 (arom *C*), 131.3, 128.7, 127.2, 126.4, 123.4, 114.3 (arom *C*H), 98.3 (C-9a), 95.0 (C-2), 40.9 (*C*H_2), 31.5 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{18}Cl_2NO_2$ 422.0715 (M+H); found 422.0720.

*4.5.9. 3,5-Dihydro-2,2-bis(4-methylphenyl)-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9g**: R=Me, X=H, Ar=4-Me-C_6H_4).* Yield 93% (Table 3, entry 8). Colorless microcrystals (from MeOH), mp 148–150 °C. IR (KBr): ν 1640 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.907.88 (1H, m, arom *H*), 7.43–7.08 (11H, m, arom H), 3.93 (2H, s, CH_2), 3.58 (3H, s, Me), 2.25 (6H, s, Me×2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 160.6 (*C*=O and *C*=C), 141.4, 140.2, 137.1 (arom *C*), 130.6, 128.7, 125.4, 122.6, 121.2, 114.1 (arom *C*H), 112.1, 107.3 (arom *C*), 95.5

(C-2), 42.3 (CH_2), 28.6 (Me), 20.6 (2C, Me×2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1852.

*4.5.10. 3,5-Dihydro-8-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9h**: R=H, X=8-Me, Ar=Ph).* Yield 44% (Table 3, entry 9). Colorless microcrystals (from MeOH), mp 269–270 °C. IR (KBr): ν 3000–2729 (NH), 1654 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 11.5 (1H, s, N*H*), 7.89–7.35 (13H, m, arom *H*), 3.88 (2H, s, CH_2), 2.59 (3H, Me) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.0, 160.3 (*C*=O and *C*=C), 144.6, 137.8, 130.9 (arom *C*), 132.3, 128.5, 127.7, 125.3, 121.2, 115.5 (arom *C*H), 110.5, 107.7 (arom *C*), 95.0 (C-2), 41.6 (CH_2), 20.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}NO_2$ 354.1494 (M+H); found 354.1505.

*4.5.11. 3,5-Dihydro-6-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9i**: R=H, X=6-Me, Ar=Ph).* Yield 67% (Table 3, entry 10). Only slightly soluble in organic solvents. Colorless microcrystals (from MeOH), mp 263–267 °C. IR (KBr): ν 3300–3000 (NH), 1670 (C=O) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.7 (1H, s, N*H*), 7.90–7.18 (13H, m, arom *H*), 3.83 (2H, s, CH_2), 2.39 (3H, Me) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.5, 165.4 (*C*=O and *C*=C), 144.4, 140.2, 139.1, 138.0, 137.0, 133.7, 132.2, 128.8, 128.4, 127.7, 127.6, 127.1, 126.1, 125.2, 124.4, 124.0, 121.9, 121.5, 119.8, 97.9, 95.1, 41.5, 17.6 ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{20}NO_2$ 354.1494 (M+H); found 354.1495.

*4.5.12. 8-Chloro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9j**: R=H, X=8-Cl, Ar=Ph).* Yield 58% (Table 3, entry 11). Colorless microcrystals (from MeOH), mp 281–283 °C. IR (KBr): ν 3150–2721 (NH), 1680 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 11.6 (1H, s, NH), 7.96 (1H, m, arom *H*), 7.61–7.58 (5H, m, arom *H*), 7.35–7.28 (7H, m, arom *H*), 3.81 (2H, CH_2) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.2, 160.1 (*C*=O and *C*=C), 144.4, 138.4, 125.8 (arom C), 131.0, 128.5, 127.7, 125.3, 121.0, 117.5 (arom *C*H), 111.7, 109.0 (arom *C*), 95.6 (C-2), 41.5 (CH_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}ClNO_2$ 374.0948 (M+H); found 374.0952.

*4.5.13. 6-Chloro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9k**: R=H, X=6-Cl, Ar=Ph).* Yield 99% (Table 3, entry 12). Only slightly soluble in organic solvents. Colorless microcrystals (from MeOH), mp 254–255 °C. IR (KBr): ν 3200–3000 (NH), 1660 (C=O) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 10.8 (1H, s, NH), 7.95–7.28 (13H, m, arom H), 3.85 (2H, s, CH_2) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 161.0, 160.2 (*C*=O and *C*=C), 144.3, 136.0, 131.3 (arom *C*), 128.6, 127.2, 126.2, 125.4, 122.6, 121.3, 118.9 (arom *C*H), 112.4, 108.9 (arom *C*), 95.8 (C-2), 41.5 (CH_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}ClNO_2$ 374.0948 (M+H); found 374.0945.

*4.5.14. 8-Fluoro-3,5-dihydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**9l**: R=H, X=8-F, Ar=Ph).* Yield 74% (Table 3, entry 13). Colorless microcrystals (from MeOH), mp 248 °C (decomp.). IR (KBr): ν 3180–2900 (NH), 1670 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 11.6 (1H, s, N*H*), 7.84–7.25 (13H, m, arom *H*), 3.81 (2H, CH_2) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.5, 160.2 (*C*=O and *C*=C), 155.3 (C-8), 144.4, 136.5 (arom *C*), 128.5, 127.7, 125.3, 119.3, 117.6, 107.2 (arom *C*H), 109.0 (arom *C*), 95.4 (C-2), 41.6 (CH_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}FNO_2$ 358.1243 (M+H); found 358.1244.

*4.5.15. 3,5-Dihydro-5-methyl-2-(2,2-diphenylethenyl)furo[3,2-c]quinolin-4(2H)-one (**9m**: R=Me, X=H, Ar=Ph).* Yield 71% (Table 3, entry 14). R_f=0.16 (Et_2O/hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 161 °C. IR (KBr): ν 1659 (C=O), 1638 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78–7.76 (1H, m, arom *H*), 7.57–7.17 (13H, m, arom *H*), 6.29 (1H, d, *J*=9.5 Hz, =C*H*–), 5.50 (1H, dt, *J*=7.7, 9.5 Hz, >C*H*–), 3.67 (3H, s, Me), 3.39 (1H, dd, *J*=15.4, 9.5 Hz, –CH_2–), 3.13 (1H, dd, *J*=15.4, 7.7 Hz, –CH_2–) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2 (*C*=O), 161.2 (–*C*O=), 146.0 (Ph_2>*C*=), 141.1, 140.5, 138.6 (arom *C*), 130.9, 129.9, 128.4, 128.3, 128.1, 128.0, 127.8, 126.5, 123.2, 121.5 (arom *C*H), 114.4 (=*C*H–), 112.6 (arom *C*), 108.0 (>*C*=), 83.5 (>CH–), 35.2 (–CH_2–), 29.0 (Me). Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.08; H, 5.53; N, 3.60.

*4.5.16. 2-[2,2-Bis(4-fluorophenyl)ethenyl]-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9n**: R=Me, X=H, Ar=4-F-C_6H_4).* Yield 58% (Table 3, entry 15). R_f=0.12 (Et_2O/hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 179–181 °C. IR (KBr): ν 1659 (C=O), 1636 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79–7.77 (1H, m, arom *H*), 7.60–7.58 (1H, m, arom *H*), 7.55–6.97 (10H, m, arom *H*), 6.23 (1H, d, *J*=9.5 Hz, =C*H*–), 5.47 (1H, dt, *J*=7.7, 9.5 Hz, >C*H*–), 3.70 (3H, s, Me), 3.41 (1H, dd, *J*=15.4, 9.5 Hz, –CH_2–), 3.13 (1H, dd, *J*=15.4, 7.7 Hz, –CH_2–) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 161.2 (*C*=O and *C*=C), 162.1 (*C*–F), 144.2 (Ph_2>*C*=), 140.6, 137.2, 137.1, 134.4, 134.3 (arom *C*), 131.7, 131.6, 131.0, 129.6, 129.5, 126.7, 123.2, 121.6, 115.7, 115.4, 115.1 (arom *C*H), 114.5 (=*C*H–), 112.5 (arom *C*), 107.9 (>*C*=), 83.3 (>CH–), 35.2 (–CH_2–), 29.1 (Me) ppm. Anal. Calcd for $C_{26}H_{19}F_2NO_2$: C, 75.17; H, 4.61; N, 3.37. Found: C, 75.16; H, 4.73; N, 3.36.

*4.5.17. 2-[2,2-Bis(4-chlorophenyl)ethenyl]-3,5-dihydro-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9o**: R=Me, X=H, Ar=4-Cl-C_6H_4).* Yield 69% (Table 3, entry 16). R_f=0.13 (Et_2O/hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 123–124 °C. IR (KBr): ν 1659 (C=O), 1636 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76–7.74 (1H, m, arom *H*), 7.59–7.53 (1H, m, arom *H*), 7.43–7.18 (10H, m, arom *H*), 6.27 (1H, d, *J*=9.5 Hz, =C*H*–), 5.45 (1H, dt, *J*=7.7, 9.5 Hz, >C*H*–), 3.68 (3H, s, Me), 3.39 (1H, dd, *J*=15.4, 9.5 Hz, –CH_2–), 3.12 (1H, dd, *J*=15.4, 7.7 Hz, –CH_2–) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 161.1 (*C*=O and -*C*O=), 143.8 (Ph_2>*C*=), 140.5, 139.2, 136.5, 134.3 (arom *C*), 131.2, 131.0, 129.0, 128.8, 128.5, 127.4, 123.1, 121.6 (arom *C*H), 114.5 (=*C*H–), 112.4 (arom *C*), 107.8 (>*C*=), 83.0 (>CH–), 35.1 (–CH_2–), 29.1 (Me) ppm. Anal. Calcd for $C_{26}H_{19}Cl_2NO_2$: C, 69.65; H, 4.27; N, 3.12. Found: C, 69.37; H, 4.18; N, 3.04.

*4.5.18. 3,5-Dihydro-2-[2,2-bis(4-methylphenyl)ethenyl]-5-methylfuro[3,2-c]quinolin-4(2H)-one (**9p**: R=Me, X=H, Ar=4-Me-C_6H_4).* Yield 71% (Table 3, entry 17). R_f=0.30 (Et_2O/hexane 8:2 v/v). Colorless microcrystals (from Et_2O), mp 160 °C. IR (KBr): ν 1657 (C=O), 1636 (C=C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79–7.76 (1H, m, arom *H*), 7.57–7.52 (1H, m, arom *H*), 7.35–7.08 (10H, m, arom *H*), 6.23 (1H, d, *J*=9.5 Hz, =C*H*–), 5.52 (1H, dt, *J*=7.7, 9.5 Hz, >C*H*–), 3.68 (3H, s, N–Me), 3.39 (1H, dd, *J*=15.4, 9.5 Hz, –CH_2–), 3.12 (1H, dd, *J*=15.4, 7.7 Hz, –CH_2–), 2.40 (3H, s, Me), 2.33 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 161.2 (*C*=O and –CO=), 145.9 (Ph_2>*C*=), 140.5, 138.5, 138.0, 137.7, 135.8 (arom *C*), 130.8, 129.9, 129.0, 128.9, 127.8, 125.4, 123.2, 121.5 (arom *C*H), 114.4 (=*C*H–), 112.6 (arom *C*), 108.0 (>*C*=), 83.8 (>CH–), 35.2 (–CH_2–), 29.0 (N–Me), 21.3 (Me), 21.1 (Me) ppm. Anal. Calcd for $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44. Found: C, 82.24; H, 6.19; N, 3.33.

*4.5.19. 3,5,6,7,8,9-Hexahydro-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**12**).* Yield 53% (Table 4, entry 1). Only slightly soluble in organic solvents. Colorless cubics (from MeOH), mp 281–283 °C. IR (KBr): ν 3200–2900 (NH), 1651 (C=O) cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ 11.05 (1H, s, N*H*), 7.50–7.48 (4H, m, arom *H*), 7.38–7.35 (4H, m, arom *H*), 7.29–7.26 (2H, m, arom *H*), 3.63 (2H, s, CH_2), 2.45 (2H, s, CH_2), 1.69 (6H, s, CH_2) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.4, 160.1 (*C*=O and –*C*O=), 144.9, 144.6 (arom *C*), 128.4, 127.5, 125.3 (arom *C*H), 104.4, 101.3 (arom *C*), 94.1 (C-2), 41.1 (CH_2), 26.0 (CH_2), 21.34 (CH_2), 21.30 (CH_2), 20.4 (CH_2) ppm. Anal. Calcd for

$C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.47; H, 6.16; N, 3.98.

*4.5.20. 5-Benzyl-3,5,6,7-tetrahydro-2,2-diphenylfuro[3,2-c]pyridin-4(2H)-one (**14**).*[4a] Yield 52% (Table 4, entry 2). Yellow oil; IR ($CHCl_3$): ν 1680 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.20 (15H, m, arom *H*), 4.58 (2H, s, Ph–CH_2), 3.67 (2H, t, *J*=2.2 Hz, H-3), 3.35 (2H, t, *J*=7.2 Hz, H-6), 2.55 (2H, tt, *J*=7.2, 2.2 Hz, H-7) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6, 164.7 (*C*=O and C-7a), 144.8, 137.9 (arom *C*), 128.6, 128.4, 128.0, 127.7, 127.3, 125.7 (arom *C*H), 104.8 (C-3a), 95.4 (C-2), 48.9 (Ph-CH_2), 44.3 (C-6), 42.0 (C-3), 23.3 (C-7). FAB HRMS (acetone/NBA): calcd for $C_{26}H_{23}NO_2$ 382.1807 (M+H); found 382.1812.

*4.5.21. 2,3-Dihydro-2,2-diphenyl-4H-furo[3,2-c][1]benzopyran-4-one (**16a**).* Yield 89% (Table 4, entry 3). Colorless microcrystals (from EtOH), mp 185–186 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87–7.84 (1H, m, arom *H*), 7.61–7.56 (1H, m, arom *H*), 7.47–7.25 (12H, m, arom *H*), 3.91 (2H, s, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0 (*C*=O), 155.1 (*C*=C), 143.5 (arom *C*), 132.4, 128.6, 128.2, 125.7, 124.0, 122.7, 117.0 (arom *C*H), 112.4 (C-9a), 101.7 (C-3a), 97.4 (C-2), 41.5 (CH_2) ppm. FAB HRMS (acetone/NBA): calcd for $C_{23}H_{17}O_3$ 341.1178 (M+H); found 341.1207.

*4.5.22. 2,2-Bis(4-chlorophenyl)-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (**16b**).* Yield 87% (Table 4, entry 4). Colorless microcrystals (from EtOH), mp 196–197 °C. IR (KBr): ν 1717 (C=O), 1651 (C=C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.83–7.81 (1H, m, arom *H*), 7.61–7.58 (1H, m, arom *H*), 7.41–7.32 (10H, m, arom *H*), 3.84 (2H, s, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7 (O–*C*=C), 159.9 (*C*=O), 155.1 (arom *C*–O), 141.6, 134.4 (arom *C*), 132.7, 128.9, 127.1, 124.1, 122.6, 117.1 (arom *C*H), 112.2 (C-9a), 101.5 (C-3a), 96.3 (C-2), 41.3 (CH_2) ppm. Anal. Calcd for $C_{23}H_{14}Cl_2O_3 \cdot 1/9H_2O$: C, 67.17; H, 3.49. Found: C, 67.03; H, 3.37.

*4.5.23. 2,3-Dihydro-2,2-bis(4-methylphenyl)-4H-furo[3,2-c][1]benzopyran-4-one (**16c**).* Yield 82% (Table 4, entry 5). Colorless needles (from EtOH), mp 121 °C. IR (KBr): ν 1719 (C=O), 1649 (C=C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.83–7.82 (1H, m, arom *H*), 7.57–7.54 (1H, m, arom *H*), 7.39–7.37 (1H, m, arom *H*), 7.33–7.31 (5H, m, arom *H*), 7.17–7.15 (4H, m, arom *H*), 3.86 (2H, s, CH_2), 2.33 (6H, s, Me×2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0 (O–*C*=C), 160.3 (*C*=O), 155.0 (arom C–O), 140.8, 138.0 (arom *C*), 132.3, 129.1, 125.7, 123.9, 122.7, 116.9 (arom *C*H), 112.5 (C-9a), 101.7 (C-3a), 97.6 (C-2), 41.45 (CH_2), 21.0 (Me×2) ppm. Anal. Calcd for $C_{25}H_{20}O_3 \cdot 1/8H_2O$: C, 81.01; H, 5.51. Found: C, 80.94; H, 5.34.

*4.5.24. 2,3-Dihydro-6-methyl-2,2-diphenyl-4H-furo[3,2-c]pyran-4-one (**18**).* Yield 56% (Table 4, entry 6). Colorless microcrystals (from MeOH), mp 151–152 °C. IR (KBr): ν 1716 (C=O), 1273 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.29 (10H, m, arom H), 6.08 (1H, s, =*C*H), 3.74 (2H, s, CH_2), 2.26 (3H, s, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7 (C-7a), 165.5 (*C*=O), 161.7 (C-6), 143.6 (arom *C*), 128.4, 1278.0, 125.6 (arom *C*H), 98.9 (C-3a), 96.8 (C-2), 95.6 (C-7), 40.2 (CH_2), 20.4 (Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{20}H_{17}O_3$ 305.1178 (M+H); found 305.1211.

*4.5.25. 6,6-Dimethyl-2-(2,2-diphenylethenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20a**).* Yield 78% (Table 4, entry 7). R_f=0.22 (Et_2O/hexane 5:5 v/v). Colorless needles (from EtOH), mp 139–141 °C. IR (KBr): ν 1647, 1626 (C=C–C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.21 (10H, m, arom *H*), 6.15 (1H, d, *J*=9.5 Hz, =*CH*–), 5.28 (1H, dt, *J*=7.7, 9.5 Hz, >*CH*–), 3.01 (1H, dd, *J*=14.3, 9.5 Hz, –CH_2–, H-3), 2.74 (1H, dd, *J*=14.3, 7.7 Hz, –CH_2–, H-3), 2.29 (2H, s, –CH_2–, H-5), 2.22 (2H, s, –CH_2–, H-7), 1.11 (3H, s, Me), 1.08 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6 (*C*=O), 176.1 (–*C*O=), 146.1 (arom *C*), 141.0 (Ph_2>*C*=), 138.5 (arom *C*), 129.8, 128.3, 128.2, 128.1, 127.9, 127.8 (arom *C*H), 126.2 (=*C*H–), 111.5 (>*C*=), 83.6 (>*C*H–), 50.9 (–CH_2–, C-5), 37.9 (–CH_2–, C-7), 34.0 (>*C*<), 32.9 (–CH_2–, C-3), 28.7 (2Me) ppm. Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.43; H, 7.01.

*4.5.26. 2-[2,2-Bis(4-fluorophenyl)ethenyl]-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20b**).* Yield 55% (Table 4, entry 8). R_f=0.18 (Et_2O/hexane 5:5 v/v). Colorless amorphous. IR (KBr): ν 1634 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.29–6.96 (8H, m, arom *H*), 6.10 (1H, d, *J*=9.5 Hz, =*CH*–), 5.240 (1H, dt, *J*=7.7, 9.5 Hz, >*CH*–), 3.02 (1H, dd, *J*=14.3, 9.9 Hz, –CH_2–, H-3), 2.73 (1H, dd, *J*=14.3, 7.7 Hz, –CH_2–, H-3), 2.31 (2H, s, –CH_2–, H-5), 2.24 (2H, s, –CH_2–, H-7), 1.12 (3H, s, Me), 1.01 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6 (*C*=O), 176.0 (–*C*O=), 164.4, 164.2, 161.1, 160.9 (arom *C*), 144.2 (Ph_2>*C*=), 137.1, 134.3, 134.2 (arom *C*), 131.6, 131.5, 129.6, 129.4 (arom *C*H), 126.5 (=*C*H–), 115.6, 115.4, 115.1 (arom *C*H), 111.5 (>*C*=), 83.3 (>*C*H–), 50.9 (–CH_2–, C-5), 37.9 (–CH_2–, C-7), 34.1 (>*C*<), 33.0 (–CH_2–, C-3), 28.7 (2Me) ppm. FAB HRMS (acetone/NBA) calcd for $C_{24}H_{23}F_2O_2$ 380.1666 (M+1). Found 381.1669.

*4.5.27. 2-[2,2-Bis(4-chlorophenyl)ethenyl]-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**20c**).* Yield 63% (Table 4, entry 9). R_f=0.22 (Et_2O/hexane 5:5 v/v). Colorless plates (from EtOH); mp 144–146 °C. IR (KBr): ν 1630 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.14 (8H, m, arom *H*), 6.14 (1H, d, *J*=9.5 Hz, =*CH*–), 5.23 (1H, dt, *J*=7.7, 9.5 Hz, >*CH*–), 3.01 (1H, dd, *J*=14.7, 9.9 Hz, –CH_2–, H-3), 2.73 (1H, dd, *J*=14.7, 7.7 Hz, –CH_2–, H-3), 2.30 (2H, s, –CH_2–, H-5), 2.23 (2H, s, –CH_2–, H-7), 1.12 (3H, s, Me), 1.09 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6 (*C*=O), 175.9 (–*C*O=), 143.9, 139.1 (arom *C*), 136.4 (Ph_2>*C*=), 134.3 (arom *C*), 131.2, 129.0, 128.8, 128.5 (arom *C*H), 127.2 (=*C*H–), 111.5 (>*C*=), 83.0 (>*C*H–), 50.9 (–CH_2–, C-5), 37.9 (–CH_2–, C-7), 34.1 (>*C*<), 32.9 (–CH_2–, C-3), 28.7 (2Me) ppm. Anal. Calcd for $C_{24}H_{22}Cl_2O_2$: C, 69.74; H, 5.36. Found: C, 69.44; H, 5.26.

*4.5.28. 7a,3a-(Epoxyethano)-6,7-dihydro-6,6-dimethyl-9-(2,2-diphenylethenyl)-2-phenylbenzofuran-4(5H)-one (**22**).* A 7:1 diastereomixture was obtained and the diastereomers could not be isolated each other. Yield 58% (Table 4, entry 10). R_f=0.43 (Et_2O/hexane 3:7 v/v). Colorless amorphous. IR ($CHCl_3$): ν 1705 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.66–7.07 (15H, m, arom *H*), 5.98 (1H, d, *J*=8.8 Hz, =*CH*–), 5.24 (1H, s, =*CH*–), 4.70–4.62 (1H, m, >*CH*–), 2.43–2.09 (6H, m, –CH_2–×3), 1.05 (3H, s, Me), 0.97 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.9 (*C*=O), 156.5 (Ph-*C*O=), 146.2 (acom *C*), 141.8 (Ph_2>*C*=), 138.7 (arom *C*), 129.7, 129.1, 128.3, 128.1, 127.8, 126.7 (arom *C*H), 125.5 (Ph_2>C=*C*H–), 118.5 (C-7a), 98.0 (C-3), 76.3 (C-9), 67.3 (C-3a), 51.7, 46.8, 43.9 (–CH_2–×3), 32.0 (C-6), 29.2, 28.7 (Me) ppm. FAB HRMS (acetone/NBA) calcd for $C_{32}H_{30}O_3$ 462.2195 (M). Found 462.2196.

*4.5.29. 3,3a,5,9b-Tetrahydro-9b-hydroxy-3a-methyl-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**23a**: R=Me, Ar=Ph).* Colorless microcrystals (from MeOH), mp 217–225 °C (decomp.). IR (KBr): ν 3500–3400 (NH), 3400–3060 (OH), 1649 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.2, (1H, s, NH), 7.92–7.90 (1H, m, arom *H*), 7.54–7.51 (2H, m, arom *H*), 7.32–6.91 (10H, m, arom *H*), 6.64 (1H, m, arom *H*), 3.73 (1H, d, *J*=11.9 Hz, *H*a-3), 3.42 (1H, s, OH), 2.96 (1H, d, *J*=11.9 Hz, *H*b-3), 2.07 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1 (*C*=O), 149.6, 147.0 (arom *C*), 135.7, 129.5, 127.8, 127.6, 126.8, 126.7, 126.1, 125.9, 125.5, 125.0, 123.5, 121.9, 102.7, 85.9 (C-2), 53.6 (C-3a), 46.7 (CH_2), 18.4 (Me) ppm. Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.46; H, 5.52; N, 3.80.

*4.5.30. 3,3a,5,9b-Tetrahydro-9b-hydroxy-2,2-diphenyl-3a-propylfuro[3,2-c]quinolin-4(2H)-one (**23b**: R=Pr, Ar=Ph).* The compound **23b**

could not be separated from **24b**. Colorless microcrystals (from MeOH), mp 220–222 °C. IR (KBr): ν 3454–2875 (OH and NH), 1689 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.76 (1H, s, N*H*), 7.71–6.66 (14H, m, arom *H*), 3.45 (2H, s, CH_2), 2.08–1.01 (4H, m, $CH_2\times2$), 2.01 (1H, s, OH), 0.86 (3H, t, J=7.0 Hz, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{25}NO_3$ 399.1834 (M); found 399.1836.

*4.5.31. 3a-Butyl-3,3a,5,9b-tetrahydro-9b-hydroxy-2,2-diphenylfuro[3,2-c]quinolin-4(2H)-one (**23c**: R=Bu, Ar=Ph).* Compound **23c** could not be separated from **24c**. Pale yellow microcrystals (from MeOH), mp 166 °C. IR (KBr): ν 3400–2900 (OH, NH), 1657 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.92 (1H, s, N*H*), 7.61–6.84 (14H, m, arom H), 2.88 (1H, d, J=13.8 Hz, *H*CH), 2.39 (1H, d, J=13.8 Hz, HC*H*), 2.37 (1H, s, O*H*), 1.28–1.07 (6H, m, $CH_2\times3$), 0.78 (3H, t, J=7.0 Hz, Me) ppm.

*4.5.32. 2,2-Bis(4-chlorophenyl)-3,3a,5,9b-tetrahydro-9b-hydroxy-3a-methylfuro[3,2-c]quinolin-4(2H)-one (**23d**: R=Me, Ar=4-Cl-C_6H_4).* Compound **23d** could not be separated from **24d**. Colorless microcrystals (from MeOH); mp 221–223 °C. IR (KBr): ν 3400–2877 (OH and NH), 1697 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 10.7 (1H, s, N*H*), 7.83–6.72 (12H, m, arm *H*), 3.40 (1H, s, O*H*), 3.53 (1H, d, J=13.0 Hz, *H*CH), 3.17 (1H, d, J=13.0 Hz, HC*H*), 1.36 (3H, s, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{24}H_{19}Cl_2NO_3$ 439.0742 (M); found 439.0648.

*4.5.33. 3-Methyl-3-(2,2-diphenylethenyl)quinoline-2,4(1H,3H)-dione (**24a**: R=Me, Ar=Ph).* Colorless microcrystals (from MeOH), mp 160–161 °C. IR (KBr): ν 3550–3400 (NH), 1701, 1655 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (1H, s, N*H*), 7.73–7.71 (1H, m, arom *H*), 7.39–7.21 (6H, m, arom *H*), 7.02–6.80 (7H, m, arom *H*), 6.42 (1H, s, *H*C=), 1.79 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.9, 175.9 (C=O), 144.5,140.8, 140.7, 138.7 (arom C), 135.6, 131.1, 129.9, 128.1, 127.7,127.6, 127.5, 127.4, 127.2, 123.0 (arom CH), 118.2 (CH=*C*), 116.2 (*C*H=C), 56.3 (C-3), 27.6 (Me) ppm. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.57; H, 5.31; N, 3.91. FAB HRMS (acetone/NBA): calcd for $C_{29}H_{22}NO_2$ 416.1651 (M+H); found 416.1638.

*4.5.34. 3-(2,2-Diphenylethenyl)-3-propylquinoline-2,4(1H,3H)-dione (**24b**: R=Pr, Ar=Ph).* Compound **24b** could not be separated from **23b**. Colorless microcrystals (from MeOH), mp 220–222 °C. IR (KBr): ν 3200–2875 (NH), 1689, 1647 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.90 (1H, s, N*H*), 7.71–6.86 (14H, m, arom *H*), 6.39 (1H, s, *H*C=), 2.37–2.34 (2H, m, CH_2), 1.50–1.00 (2H, m, CH_2), 0.79 (3H, t, J=5.5 Hz, Me) ppm. FAB HRMS (acetone/NBA): calcd for $C_{26}H_{24}NO_2$ 382.1807 (M+H); found 382.1885.

*4.5.35. 3-Butyl-3-(2,2-diphenylethenyl)quinoline-2,4(1H,3H)-dione (**24c**: R=Bu, Ar=Ph).* Compound **24c** could not be separated from **23c**. Pale yellow microcrystals (from MeOH), mp 166 °C. IR (KBr): ν 3250–2869 (NH), 1697, 1656 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.92 (1H, s, N*H*), 7.71–7.68 (1H, m, arom *H*), 7.34–7.32 (1H, m, arom *H*), 7.26–7.21 (5H, m, arom *H*), 7.01–6.98 (1H, m, arom *H*), 6.92–6.84 (5H, m, arom *H*), 6.73–6.70 (1H, m, arom *H*), 6.40 (1H, s, vinyl *H*), 2.39 (2H, t, J=5.8 Hz), 1.28–1.19 (4H, m, $CH_2\times2$), 0.757 (3H, t, J=6.4 Hz, Me) ppm. HRMS (acetone/NBA): calcd for $C_{267}H_{26}NO_2$ 396.1964 (M+H); found 396.1884.

*4.5.36. 3-[2,2-Bis(4-chlorophenyl)ethenyl]-3-methylquinoline-2,4(1H,3H)-dione (**24d**: R=Me, Ar=4-Cl-C_6H_4).* Compound **24d** could not be separated from **23d**. Colorless microcrystals (from MeOH), mp 221–223 °C. IR (KBr): ν 3200–2877 (NH), 1697, 1658 (C=O) cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 10.2 (1H, s, N*H*), 7.83–6.72 (12H, m, arom *H*), 6.46 (1H, s, =C*H*), 1.60 (3H, s, Me) ppm. HRMS (acetone/NBA): calcd for $C_{24}H_{18}Cl_2NO_2$ 422.0715 (M+H); found 422.0715.

*4.5.37. 3-[2,2-Bis(4-methylphenyl)ethenyl]-3-methylquinoline-2,4(1H,3H)-dione (**24e**: R=Me, Ar=4-Me-C_6H_4).* Colorless microcrystals (from MeOH), mp 160–161 °C. IR (KBr): ν 3260–2868 (NH), 1678, 1654 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (1H, s, N*H*), 7.66–7.64 (1H, m, arom *H*), 7.39–7.34 (1H, m, arom *H*), 7.19–7.16 (2H, m, arom *H*), 7.05–6.95 (3H, m, arom *H*), 6.80–6.73 (3H, m, arom *H*), 6.66–6.63 (2H, m, arom *H*), 6.39 (1H, s, *H*C=), 2.30 (3H, s, Me), 1.98 (3H, s, Me), 1.78 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.0, 176.3 (C=O), 144.3 (*C*=CH), 140.8, 138.0, 137.5, 137.0, 136.0 (arom *C*), 135.2, 130.8, 129.9, 128.7, 128.3, 127.4, 127.0, 122.8 (arom *C*H), 118.3 (arom *C*), 116.0 (*C*H=C), 56.3 (C-3), 27.4, 21.1, 20.9 (Me) ppm. Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.78; H, 6.01; N, 3.70.

Acknowledgements

This research was supported by Grants-in-Aid for Scientific Research (C), No. 22550041 and No. 25410049, from the Japan Society for the Promotion of Science, and also by a 2013-Core Research Program, 'Integrated Science for Molecular Chirality in Biology and Chemistry,' Graduate School of Science and Technology, Kumamoto University, Japan. We gratefully acknowledge Professor Teruo Shinmyouzu and Dr. Mikio Yasutake, Institute for Materials Chemistry and Engineering, Kyushu University, Japan, for the measurement of the X-ray analysis. We also acknowledge Nissan Chemical Industries, Ltd., and M.Y. thanks the Scientific and Technological Research Council of Turkey, TUBITAK No. 2214, for their financial support.

Supplementary data

X-ray data of **3b** (R=Me, Ar^1=Ar^2=4-Cl-C_6H_4) and **4a** (R=Me, Ar^1=Ar^2=Ph), ^1H NMR, ^{13}C NMR, and also DEPT-135 spectra of the products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.01.013.

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