A Synthesis of 1-Azaanthraquinones *via* Diels–Alder Reaction of 4-Hydroxy- and 4-Methoxy-2-phenylquinolinequinones with 3-Trimethylsilyloxy-1,3-butadienes: Observation of Inverse Regioselectivity

Yoshie HORIGUCHI, Akio TOEDA, Katuhiro TOMODA, Hideki SUZUKI, and Takehiro SANO*

Showa College of Pharmaceutical Sciences, Machida-shi, Tokyo 194–8543, Japan.
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Diels–Alder reaction of 4-hydroxy-2-phenylquinolinequinone (10a) and 4-methoxy-2-phenylquinolinequinone (10b) with 1-methoxy-3-trimethylsilyloxybutadiene proceeded in a highly regio- and stereoselective manner to give the [4+2] adducts (11) and (14) in good yields, respectively. The structures of the adducts and their derivatives were unambiguously determined by spectroscopic data, including high resolution heteronuclear multi bond correlation. The quinolinequinones (10a and 10b) gave inverse regioselectivity. This is related to the presence of the hydroxy group or the methoxy group at the C-4 position. These results demonstrated that Diels–Alder reaction of azadienophiles with activated dienes provides a versatile method for synthesizing 4-oxygenated 1-azaanthraquinones.

Key words Diels–Alder reaction; quinolinequinone; regioselectivity; 1-methoxy-3-trimethylsilyloxybutadiene; 1-azaanthraquinone

4-Hydroxy-1-azaanthraquinone (4-hydroxybenzo[*g*]quinoline-5,10-dione) (**1**) can be considered to have potential anticancer activity due to close structural analogy with metoxantrone (**2**), an anthraquinone anticancer agent in clinical use.[1] Quinolinequinone (quinoline-5,8-dione) (**3**) has been recognized as a classical azadienophile.[2] Recently, Potts *et al.*, synthesized various substituted 1-azaanthraquinones *via* Diels–Alder reaction of the azaquinone (**3**) with a variety of 1,3-dienes and observed that cycloaddition with unsymmetric dienes proceeded in a regioselective manner.[3] For example, the reaction of **3** with 1-methoxy-3-trimethylsilyloxy-1,3-butadiene gave 7-acetoxy-1-azaanthraquinone (**5**) as the sole product after acetylation of the Diels–Alder adduct (**4**), which was not isolated in a pure form.

In Diels–Alder reactions of 5-oxy-1,4-naphthoquinone (**6**) with unsymmetric 1,3-dienes, the regiochemistry is known to change depending on the oxy-substituent at the 5-position.[4] Thus, the 5-hydroxy analog (**6a**) and the 5-acetoxy derivative (**6b**) gave the regioisomeric adducts (**7**) and (**8**) as a major products, respectively.[5] In this paper we describe the Diels–Alder reaction of 4-hydroxy-2-phenylquinolinequinone (**10a**) and 4-methoxy-2-phenylquinolinequinone (**10b**) with 3-trimethylsilyloxy-1,3-butadienes, in an attempt to reveal the factors controlling the regiochemistry of this reaction.

Results and Discussion

The azadienophiles employed in this study, 4-hydroxy-2-phenylquinolinequinone (**10a**) and 4-methoxy-2-phenylquinolinequinone (**10b**), were prepared by cerium ammonium nitrate (CAN) oxidation of 4-hydroxy-5,8-dimethoxyquinoline (**9a**) and 4,5,8-trimethoxyquinoline (**9b**), respectively (Chart 1). 4-Hydroxyquinoline (**9a**) was prepared starting from ethyl benzoylacetate and 2,5-dimethoxyaniline in excellent overall yield.[6] Methylation of **9a** with methyl iodide in the presence of potassium carbonate in *N*,*N*-dimethylformamide (DMF) gave the 4-methoxy derivative (**9b**).

Diels–Alder Reaction of 4-Hydroxy-2-phenylquinolinequinone (10a) with 1-Methoxy-3-trimethylsilyloxybutadiene Heating **10a** with 1-methoxy-3-trimethylsilyloxybutadiene in benzene at 120 °C for 30 min in a sealed tube under argon atmosphere gave the adduct (**11**) as a single product in 60% yield. The ^{1}H-NMR spectrum exhibited new signals attributable to an trimethylsilyloxy (OTMS) group (δ 0.30), an OMe group (δ 2.99), two methylene protons (δ 2.26, 9α-H; δ 3.20, 9β-H), three methine protons (δ 3.33, 5a-H; δ 3.46, 9a-H; δ 4.21, 6-H), and an olefinic proton (δ 5.20), indicating that the product was the desired [4+2] adduct. The ^{13}C-NMR spectrum of **11**, shown in Table 1, also supported this structural assignment. In order to obtain further structural evidence we next converted the adduct into several derivatives.

The C ring of **11** was readily aromatized by heating in toluene in the presence of silica gel and acetylation of the resulting crude product gave 4,8-diacetoxy-2-phenyl-1-azaanthraquinone (**12b**) (46% yield). The acetate was converted into the 4,8-dimethoxy derivative (**12c**) by hydrolysis with 5% HCl, followed by methylation.

When **11** was treated with lithium borohydride in tetrahydrofuran (THF), enolization of the ketone moieties on the B ring was the only observed process to give the 6-methoxy-4,5,8,10-tetraacetate (**13**) after acetylation. All protons and carbons in the products were unambiguously assigned by measurement of H–H correlation spectroscopy (COSY), C–H COSY, and 2D-nuclear Overhauser and exchange spectroscopy (NOESY) spectra. The high resolution heteronuclear multiple bond correlation (HR-HMBC) spectrum of diacetate (**12b**) revealed the connections from 3-H to 7-H (the framework of the bold line shown in Fig. 1), thus indicating that the acetate on the C ring, which originated from the diene moiety, was positioned at C-8.

Diels–Alder Reaction of 4-Methoxy-2-phenylquinolinequinone (10b) with 1-Methoxy-3-trimethylsilyloxybutadiene Diels–Alder reaction of **10b** with the diene was carried out under similar conditions described above to give adduct (**14**) as the sole product in 60% yield. The ^{1}H- and ^{13}C-NMR spectra (Table 1) were consistent with a [4+2] adduct. The

* To whom correspondence should be addressed.

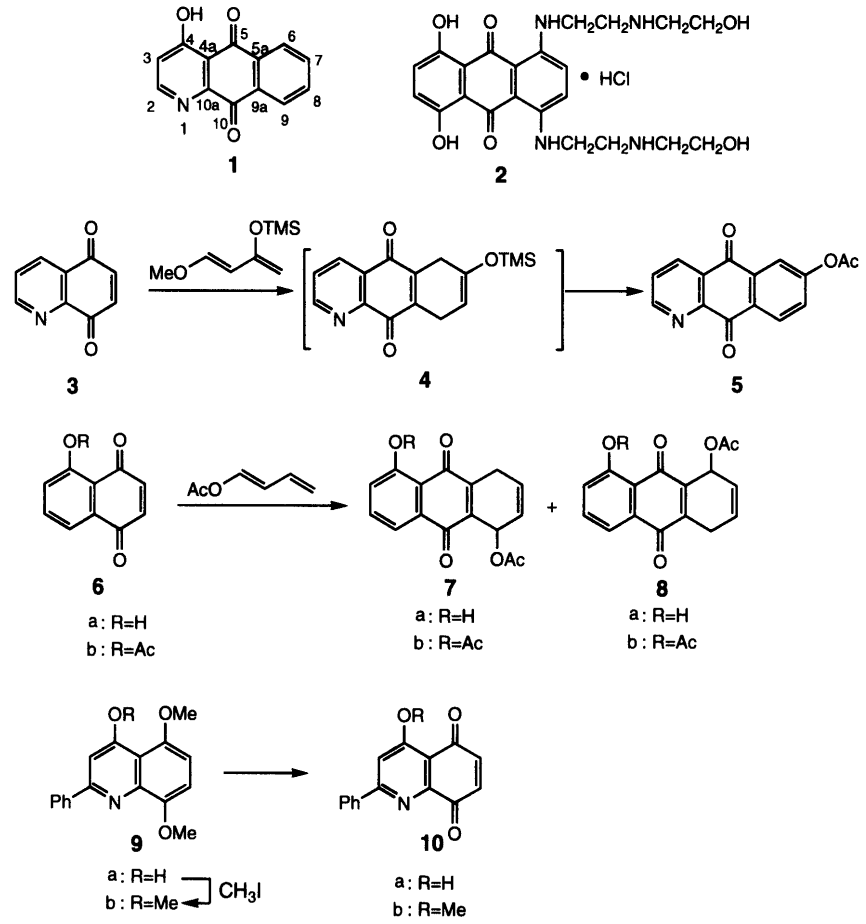

Chart 1

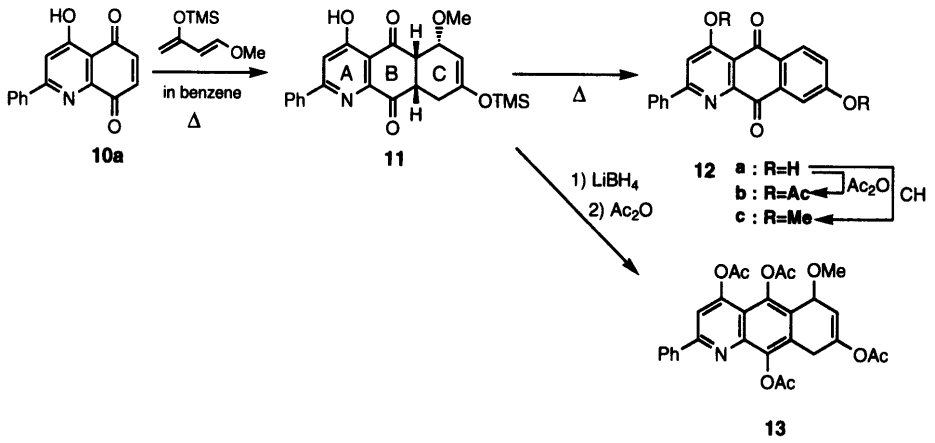

Chart 2

spectra also suggested that addition of the diene proceeded in an *endo*-manner, as judged from coupling constants between the ring juncture protons (J_{5a-9a}=6 Hz), and from the 9-proton adjacent to OMe (J_{8-9a}=4 Hz). The regiochemistry of this addition was clarified from the spectroscopic data of derivatives, as follows.

When **14** was heated in toluene in the presence of silica gel at 120 °C for 4 h, aromatization of the C ring also occurred to give monoacetate (**15b**) after acetylation of the reaction product (**15a**). This acetate was converted into 4,6-dimethoxy derivative (**15c**) by hydrolysis followed by methylation of **15a** with methyl iodide under phase-transfer (tetra-*n*-butylammonium bromide (TBAB)) conditions.

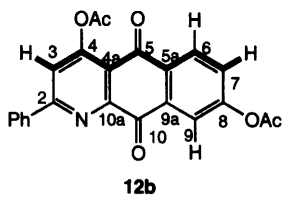

Fig. 1. C–H Four Bond Long-Range Correlation in HMBC Spectrum of **12b** in $CDCl_3$

Furthermore, reaction of **15b** with sodium borohydride in THF caused reduction of the 5,10-ketones to give triacetate (**16**) in 73% yield, after acetylation of the crude product. The

Table 1. ^{13}C-NMR Chemical Shifts of 1-Azaanthracene Ring Carbons

Aduucts	Ring numbers												
	2	3	4	4a	5	5a	6	7	8	9	9a	10	10a
11	154.5	101.3	167.8	117.1	204.8	52.0	73.9	111.2	154.4	26.5	44.2	193.2	162.7
12b	150.9	119.4	158.7	121.3	180.5	131.0	129.3	128.1	155.4	120.4	134.4	180.2	163.6
12c	151.5	106.8	167.1	118.7	182.1	126.2	129.8	120.8	163.0	110.0	137.9	180.8	164.7
14	154.2	101.6	165.4	122.8	196.3	45.0	26.6	153.1	106.6	75.1	50.8	193.4	162.1
15b	155.6	107.1	167.2	118.7	181.0	130.0	127.2	151.1	120.0	129.4	135.9	180.9	163.1
15c	151.4	106.8	167.1	118.6	182.0	126.1	120.7	162.9	110.0	129.8	137.9	180.7	164.7
16	150.2	101.9	164.2	114.9	68.7	139.1	123.1	157.1	122.3	126.6	134.8	64.7	159.0
19a	154.7	102.2	165.6	116.7	67.3	32.6	27.3	70.8	34.2	77.6	35.9	70.8	158.7
20	150.5	100.1	168.4	115.5	144.0	123.0	32.8	139.3	106.7	70.2	124.4	141.9	157.7
21	160.7	102.5	165.8	116.6	192.5	46.2	39.4	205.9	44.4	76.3	43.7	69.9	160.4

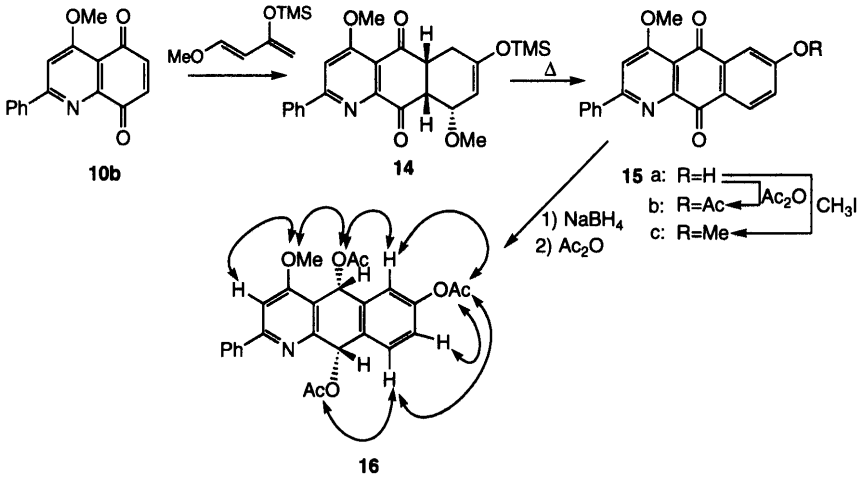

Chart 3

cross peaks observed in the 2D-NOESY of **16** revealed correlation between the 3-aromatic proton (δ 7.23) and the 7-OAc (δ 2.41), through the signals for the 4-OMe (δ 4.01), 5-OAc (δ 2.00), and the 6-aromatic proton (δ 7.4—7.6), thus establishing the location of 7-OAc. Further correlations were observed from 7-OAc to 10-OAc through two aromatic protons (δ 7.17, H-8 and δ 7.58, H-9) as shown in Chart 3. This observation strongly suggested that the Diels–Alder reaction of **10b** with the diene occurred with reverse regiochemistry to that of **10a**. In fact, the ^{1}H- and ^{13}C-NMR spectral data of 4,6-dimethoxy derivative (**15c**) were very similar, but clearly different, from those of the 4,7-dimethoxy derivative (**12c**) derived from the adduct (**11**), establishing that the compounds **12c** and **15c** were regioisomeric (see Table 1 and Experimental section).

In order to obtain more direct information regarding the stereo- and regiochemistries of the Diels–Alder reaction, several derivatives were prepared as follows. Careful hydrolysis of **14** with 5% HCl at room temperature induced selective cleavage of the OTMS group to give 5,7,10-triketone (**17**) in 75% yield. Reduction of **17** with sodium borohydride, followed by acetylation of the crude trihydroxy derivative (**18**) gave a 3 : 1 stereoisomeric mixture of the triacetate (**19**) in 64% yield. The major product (**19a**) was isolated in pure form by repeated recrystallization. Direct acetylation of triketone (**17**) caused aromatization of the B ring together with enolization of the 7-ketone to give triacetate (**20**) in 18% yield. The 2D-NOESY spectrum of **19a** indicated that

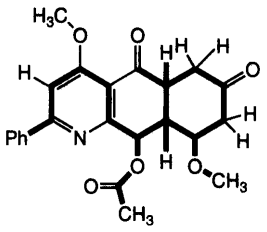

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Fig. 2. C–H Four Bond Long-Range Correlation in HMBC Spectrum of **21** in $CDCl_3$

the signal for 3-H was correlated to the signal for 7-OAc through the signals of 4-OMe and 5-OAc. This observation supported the regiochemistry of the adduct (**14**) described above. Furthermore, observation of a cross peak between the 7-OAc and 9-OMe indicated that the stereochemistries of the 7-OAc, 10-OAc, and 9-OMe groups of **19a** are all *cis*.

Confirmatory evidence about the regiochemistry of **14** was obtained from the HR-HMBC spectrum of the 5,7-dioxo-10-acetate (**21**) which was obtained by lithium borohydride reduction of **14** followed by acetylation. The spectrum clearly revealed that compound **21** has the framework shown by a bold line in Fig. 2, thus establishing not only the positions of the two ketones as C-5 and C-7, but also the position of OAc as C-10. The stereochemistry of 10-OAc was determined by the observation of nuclear Overhauser effect (NOE) between the 10-H and 5a-H as shown in chart 4, which indicated the

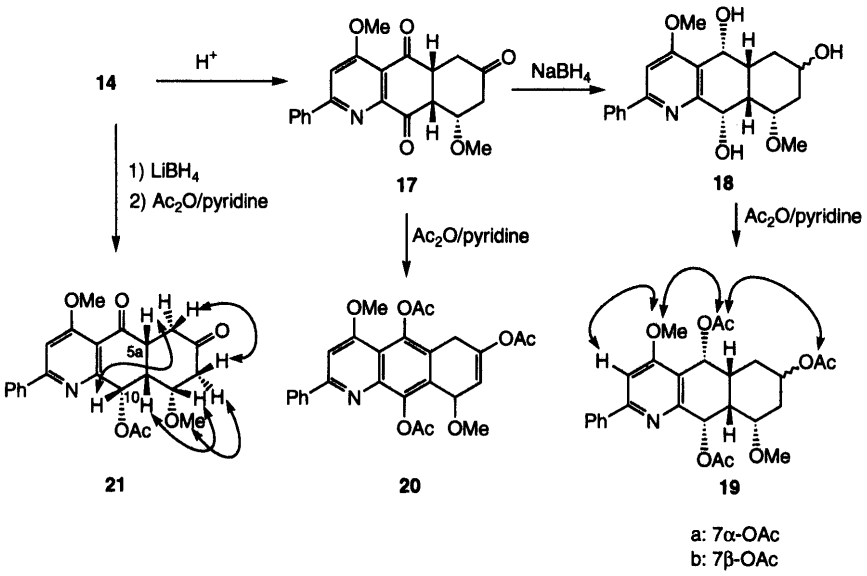

Chart 4

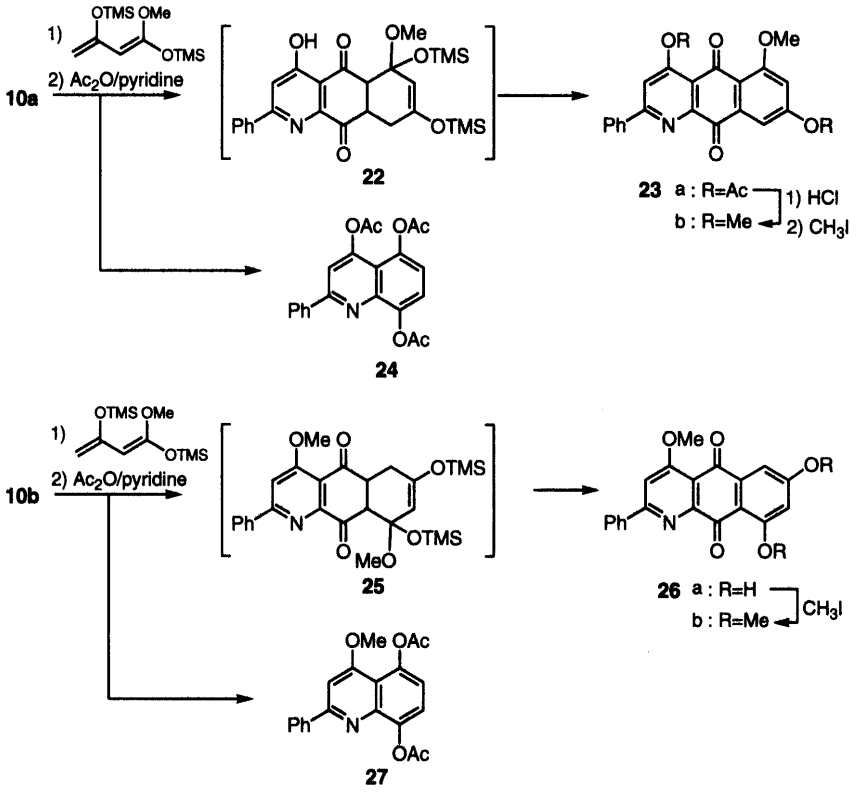

Chart 5

cis-stereochemistry.

Diels–Alder Reaction of 4-Hydroxy-2-phenylquinolinequinone (10a) and Methoxy-2-phenylquinolinequinone (10b) with 1-Methoxy-1,3-bis(trimethylsilyloxy)butadiene For synthesis of more higly oxysubstituted 1-azaanthraquinones, we examined Diels–Alder reaction of the azaquinones (**10a** and **10b**) with 1-methoxy-1,3-bis(trimethylsilyloxy)butadiene.[7] The reaction of **10a** gave 4,8-diacetoxy-6-methoxyanthraquinone (**23a**) (31% yield) together with hydroquinone triacetate (**24**) (10% yield) after the crude products were treated with 5% HCl followed by acetylation. The relative low yield of **23a** seems to be attributable to reduction of the quinone (**10a**) under the reaction conditions.[8] In fact reduction of **10a** with sodium hydrosulfite followed by acetylation gave the triacetate (**24**) in 73% yield. The diacetate (**23a**) was converted into 4,6,8-trimethoxy derivative (**23b**) by hydrolysis followed by methylation with methyl iodide.

The Diels–Alder reaction of **10b** with the diene followed by treatment of the crude products with acetic anhydride gave 7,9-dihydroxy-4-methoxy-1-azaanthraquinone (**26a**) (33%)[9] together with the hydroquinone derivative (**27**). Methylation of the dihydroxy derivative (**26a**) with methyl iodide gave the 4,7,9-trimethoxy-1-azaanthraquinone (**26b**) in 75% yield. The ^{1}H-NMR spectra of the trimethoxy-1-aza-

anthraquinones (**24b** and **26b**) were very similar, but clearly different, indicating that these compounds are regioisomeric to each other. Assignment of their regiochemistries followed from analogy to the results obtained in the reactions with 1-methoxy-3-trimethylsilyloxybutadiene.

Diels–Alder reaction of 4-hydroxy-2-phenylquinolinequinone (**10a**) and 4-methoxy-2-phenylquinolinequinone (**10b**) with 1-methoxy-3-trimethylsilyloxybutadiene was found to proceed in a highly regio- and stereoselective manner. The diene exclusively added to the azaquinones in an *endo*-fashion. The dienophilic activity of the azaquinones seemed to be relatively low, since reaction with 3-trimethylsilyloxy-1,3-butadiene did not occur. Interestingly, the regioselectivity of the azaquinones was completely reversed. The regiochemistry in the Diels–Alder reaction of non-substituted quinolinequinone (**3**)[2] is identical with that of 4-methoxyquinolinequinone (**10b**), but is opposite to that of 4-hydroxy derivative (**10a**).

In the quinolinequinone, the carbonyl group at the 8-position has more ketonic properties than the CO at the 5-position, since the latter is part of a vinylogous amide. This makes the carbon at C-6 more electrophilic than that at C-7, which determines the regiochemistry observed in the Diels–Alder reactions, for example **3**[2] and **10b**. On the other hand, inversion of the regioselectivity due to the presence of a 4-hydroxy group seems to be attributable to hydrogen bonding between the 4-OH and 5-CO, which polarizes the C=O bond at the 5-position more than that at 8-position. This electronic effect makes the carbon at C-7 more electrophilic than that at C-6, thus determining the regiochemistry of the Diels–Alder reaction of **10a**.

In conclusion these results demonstrate that the 4-oxyquinolinequinone acts as an azadienophile and that Diels–Alder reaction with electron rich 1,3-butadienes provides a versatile method for the synthesis of 4-oxygenated 1-azaanthraquinones.

Experimental

Unless otherwise stated, the following procedures were adopted. All melting points were measured on a Yanagimoto micro hot-stage melting point apparatus (Yanagimoto MP type) and are uncorrected. IR spectra were measured with a JASCO FT/IR-5000 as KBr disks or Nujol mulls and values are given in cm^{-1}. UV spectra were measured with a Hitachi U-3200 spectrophotometer in dioxane and values are given in λ_{max} nm (ε). NMR spectra were recorded on a JEOL JNM-α500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) or a JNM-AL-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) NMR spectrometer in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard. The chemical shifts are given in δ values. HR-HMBC spectra were recorded on a JEOL JNM-α500 [Δ_2 (delay time of pulse)=300 ms, J=1.7 Hz]. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were determined on a JEOL JMS-HX110A spectrometer at 30 eV with a direct inlet system. Elemental analyses were recorded on a Yanaco CHN-corder MT-3. For column chromatography, silica gel (Mallinkroft type 150A or Wako-gel C-200) was used. Thin layer chromatography (TLC) was performed on Merck precoated Silica gel 60 F254 plates. All organic extracts were washed with 5% HCl, 5% $NaHCO_3$, and water, and dried over Na_2SO_4 before concentration *in vacuo*.

Methylation of 4-Hydroxy-5,8-dimethoxy-2-phenylquinoline (9a) A suspension of **9a** (1 g), K_2CO_3, (1 g, 4 mol eq), and excess CH_3I in DMF (20 ml) was stirred at room temperature for 3 h. The reaction mixture was filtered, and the filtrate was extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=4 : 1) to give 4,5,8-trimethoxy-2-phenylquinoline (**9b**) (0.75 g, 71%) as colorless prisms from $CHCl_3$–Et_2O, mp 155—157 °C. IR: 1613, 1597, 1566, 1518. UV: 271 (37000), 340 (6000). ^{1}H-NMR: 3.94 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 4.11 (3H, s, OCH_3), 6.79 (1H, d, J=9 Hz, 6 or 7-H), 6.99 (1H, d, J=9 Hz, 6 or 7-H), 7.4—8.2 (6H, m, Ph and 3-H). *Anal.* Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.11; H, 5.86; N, 4.87.

CAN Oxidation of 4-Hydroxy-5,8-dimethoxy-2-phenylquinoline (9a) CAN (1.08 g, 2.75 mol eq) in CH_3CN–H_2O (2 : 1, 6 ml) was added to a solution of **9a** (200 mg) in CH_3CN–H_2O (2 : 1, 10 ml) with stirring at 0 °C for 20 min. The reaction mixture was then extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=4 : 1) to give 4-hydroxy-2-phenylquinoline-5,8-dione (**10a**) (145 mg, 81%) as yellow needles from Et_2O, mp 142—145 °C. IR: 1688, 1649, 1605, 1555. UV: 276 (29100), 373 (7000). ^{1}H-NMR: 6.99 (1H, d, J=10 Hz, 6 or 7-H), 7.14 (1H, d, J=10 Hz, 6 or 7-H), 7.5—8.2 (6H, m, Ar and 3-H). *Anal.* Calcd for $C_{15}H_9NO_3$: C, 71.71; H, 3.61; N, 5.57. Found: C, 71.55; H, 3.87; N, 5.38.

CAN Oxidation of 4,5,8-Trimethoxy-2-phenylquinoline (9b) CAN (1.16 g, 2.75 mol eq) in CH_3CN–H_2O (2 : 1, 6 ml) was added to a solution of **9b** (500 mg) in CH_3CN–H_2O (2 : 1, 10 ml) with stirring at 0 °C for 20 min. The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=4 : 1) to give 4-methoxy-2-phenylquinoline-5,8-dione (**10b**) (432 mg, 96%) as yellow prisms from Et_2O, mp 166—168 °C. IR: 1682, 1659, 1615, 1580, 1541. UV: 270 (26900), 354 (5800). ^{1}H-NMR: 4.14 (3H, s, OCH_3), 6.88 (1H, d, J=10 Hz, 6 or 7-H), 7.04 (1H, d, J=10 Hz, 6 or 7-H), 7.4—8.2 (6H, m, Ph and 3-H). LRMS *m/z*: 265 (M^+). HRMS *m/z* (M^+): Calcd for $C_{16}H_{11}NO_3$: 265.0737. Found: 265.0717.

Diels–Alder Reaction of 10a with 1-Methoxy-3-trimethylsilyloxy-1,3-butadiene A solution of **10a** (100 mg) and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (206 mg, 3 mol eq) in benzene (5 ml) was heated at 120 °C for 30 min in a sealed tube. After removal of the solvent *in vacuo*, the product was crystallized from $CHCl_3$–Et_2O to give (5a*S**,6*R**,9a*S**)-5a,6,9,9a-tetrahydro-4-hydroxy-6-methoxy-2-phenyl-8-trimethylsilyloxybenzo[*g*]-quinoline-5,10-dione (**11**) (98 mg, 60%) as colorless needles, mp 140—142 °C. IR: 1721, 1642. UV: 263 (12100), 308 (14600). ^{1}H-NMR: 0.30 (9H, s, OTMS), 2.26 (1H, dd, J=18, 7 Hz, 9α-H), 2.99 (3H, s, 6-OCH_3), 3.20 (1H, d, J=18 Hz, 9β-H), 3.33 (1H, dd, J=6, 4 Hz, 5a-H), 3.46 (1H, dd, J=7, 6 Hz, 9a-H), 4.21 (1H, dd, J=6, 4 Hz, 6β-H), 5.20 (1H, d, J=6 Hz, 7-H), 7.4—8.1 (6H, m, Ph and 3-H). ^{13}C-NMR: 2.50 (OTMS), 26.5 (C9), 44.2 (C9a), 52.0 (C5a), 55.0 (C6-OCH_3), 73.9 (C6), 101.3 (C3), 111.2 (C7), 117.1 (C4a), 127.7 (C3′ and C5′), 128.8 (C2′ and C6′), 130.6 (C4′), 137.5 (C1′), 154.4 (C8), 154.5 (C2), 162.7 (C10a), 168.7 (C4), 193.2 (C10), 204.8 (C5). LRMS *m/z*: 423 (M^+). HRMS *m/z* (M^+): Calcd for $C_{23}H_{25}NO_5$ Si: 423.1501. Found: 423.1506.

Preparation of 4,8-Diacetoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (12b) A suspension of **11** (100 mg) in toluene (10 ml) was heated at 120 °C in the presence of small amount of silica gel in a sealed tube for 30 min. After removal of the solvent *in vacuo*, the residue was treated with acetic anhydride–pyridine (2 : 1) (2 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was passed through a short column of silica gel. Elution with $CHCl_3$ and crystallization from $CHCl_3$ gave **12b** (44 mg, 46%) as yellow needles, mp 226—228 °C. IR: 1773, 1696, 1665. UV: 271 (15600). ^{1}H-NMR: 2.38 (3H, s, $OCOCH_3$), 2.55 (3H, s, $OCOCH_3$), 7.5—7.6 (3H, m, Ph), 7.57 (1H, dd, J=9, 2 Hz, 7-H), 7.78 (1H, s, 3-H), 8.06 (1H, d, J=2 Hz, 9-H), 8.18—8.21 (2H, m, Ph). 8.28 (1H, d, J=9 Hz, 6-H). ^{13}C-NMR: 21.1 (C4-OCO<u>C</u>H$_3$), 21.2 (C8-OCO<u>C</u>H$_3$), 119.4 (C3), 120.4 (C9), 121.3 (C4a), 127.8 (C3′ and C5′), 128.1 (C7), 129.1 (C2′and C6′), 129.3 (C6), 131.0 (C5a), 131.3 (C4′), 134.4 (C9a), 136.7 (C1′), 150.9 (C2), 155.4 (C8), 158.7 (C4), 163.6 (C10a), 168.5 (C4 and C8-O<u>C</u>OCH$_3$), 180.2 (C10), 180.5 (C5). LRMS *m/z*: 401 (M^+). HRMS *m/z* (M^+): Calcd for $C_{23}H_{15}NO_6$: 401.0907. Found: 401.0915.

Preparation of 4,8-Dimethoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (12c) A solution of **12b** (200 mg) and conc. HCl (2 ml) in dioxane–water (3 : 1) (3 ml) was refluxed for 30 min. The reaction mixture was then extracted with $CHCl_3$. The residue (130 mg) in THF (30 ml) was treated with excess CH_3I in the presence of KOH (238 mg, 8.8 mol eq) and TBAB (276 mg, 3.2 mol eq) at room temperature for 12 h under an Ar atmosphere. After removal of insoluble precipitates by filtration, the filtrate was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **12c** (110 mg, 64%) as yellow prisms from $CHCl_3$, mp 274—275 °C. IR: 1773, 1736, 1719, 1686, 1657, 1638. UV: 221 (18000), 281 (39000). ^{1}H-NMR: 3.99 (3H, s, OCH_3), 4.18 (3H, s, OCH_3), 7.29 (1H, dd, J=9, 3 Hz, 7-H), 7.5—7.6 (4H, m, Ph and 3-H), 7.74 (1H, d, J=3 Hz, 9-H), 8.1—8.2 (2H, m, Ph), 8.23 (1H, d, J=9 Hz, 6-H). ^{13}C-NMR: 55.9 (C4-OCH_3), 56.7 (C8-OCH_3), 106.8 (C3), 110.0 (C9), 118.7 (C4a), 120.8 (C7), 126.2 (C5a), 127.8 (C3′ and C5′), 129.0 (C2′ and C6′), 129.8 (C6), 130.7 (C4′), 136.4 (C1′), 137.9 (C9a), 151.5 (C2), 163.0 (C8), 164.7 (C10a), 167.1 (C4), 180.8 (C10), 182.1 (C5). LRMS *m/z*: 345 (M^+). HRMS *m/z* (M^+): Calcd for $C_{21}H_{15}NO_4$: 345.1002. Found: 345.1019.

Preparation of 4,5,8,10-Tetraacetoxy-6,9-dihydro-6-methoxy-2-phenyl-

benzo[*g*]quinoline (13) Crude **11** was obtained from reaction of **10a** (100 mg) and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (206 mg, 3 mol eq) in benzene (5 ml), as described above. $LiBH_4$ (10 mg) was added to a solution of **11** in THF (5 ml) at −60 °C and the mixture was stirred for 30 min at the same temperature. After decomposition of excess hydride with water, the reaction mixture was extracted with $CHCl_3$. The residue was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 13 h. The reaction mixture was extracted with $CHCl_3$. The residue was crystallized from $CHCl_3$–Et_2O to give **13** (49 mg, 22%) as yellow needles, mp 239—242 °C. IR: 1774, 1765, 1686, 1595. UV: 232 (16400). ^{1}H-NMR (60 °C): 2.21 (3H, s, 5-OCOCH$_3$), 2.38 (3H, s, 10-OCOCH$_3$), 2.41 (3H, s, 4-OCOCH$_3$), 2.52 (3H, s, 8-OCOCH$_3$), 2.77 (1H, dd, *J*=18, 2 Hz, 9-H), 2.95 (1H, ddd, *J*=18, 5, 3 Hz, 9-H), 3.23 (3H, s, 6-OCH$_3$), 4.78 (1H, br s, 6-H), 6.70 (1H, d, *J*=3 Hz, 7-H), 7.4—7.5 (3H, m, Ph), 7.56 (1H, s, 3-H), 8.0—8.1 (2H, m, Ph). ^{13}C-NMR (50 °C, PD=5 sec): 20.8 (OCO<u>C</u>H$_3$), 21.1 (OCO<u>C</u>H$_3$), 21.2 (2×OCO<u>C</u>H$_3$), 30.1 (C9), 48.5 (6-OCH$_3$), 70.0 (C5), 107.3 (C7), 113.0 (C3), 122.5 (C4a), 127.1 (C8), 127.6 (C3′ and C5′), 128.8 (C2′ and C6′), 130.1 (C4′), 138.4 (C1′), 140.9 (C5a), 141.3 (C9a), 143.9 (C10), 145.7 (C5), 151.4 (C10a), 154.1 (C2), 158.5 (C4), 167.7 (O<u>C</u>OCH$_3$), 168.3 (O<u>C</u>OCH$_3$), 168.8 (O<u>C</u>OCH$_3$), 168.9 (O<u>C</u>OCH$_3$). LRMS *m/z*: 520 (M^+). HRMS *m/z* (M^+): Calcd for $C_{28}H_{25}NO_9$: 519.1521. Found: 519.1542.

Diels–Alder Reaction of 10b with 1-Methoxy-3-trimethylsilyloxy-1,3-butadiene A solution of **10b** (200 mg) and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (390 mg, 3 mol eq) in benzene (5 ml) was heated at 120 °C for 30 min in a sealed tube. After removal of the solvent *in vacuo*, the product was crystallized from $CHCl_3$–Et_2O to give (5a*R**,9*S**,9a*R**)-5a,6,9,9a-tetrahydro-4,9-dimethoxy-7-trimethylsilyloxy-2-phenylbenzo[*g*]quinoline-5,10-dione (**14**) (197 mg, 60%) as colorless prisms, mp 148—150 °C. IR: 1702, 1671, 1578, 1543. UV: 263 (11100), 307 (13700). ^{1}H-NMR: 0.30 (9H, s, OTMS), 2.20 (1H, dd, *J*=18, 7 Hz, 6*β*-H), 2.97 (3H, s, 9-OCH$_3$), 3.08 (1H, d, *J*=18 Hz, 6*α*-H), 3.35 (1H, dd, *J*=6, 4 Hz, 9a-H), 3.49 (1H, dd, *J*=7, 6 Hz, 5a-H), 4.08 (3H, s, 4-OCH$_3$), 4.25 (1H, dd, *J*=6, 4 Hz, 9*β*-H), 5.19 (1H, d, *J*=6 Hz, 8-H), 7.46 (1H, s, 3-H), 7.5—8.1 (5H, m, Ph). ^{13}C-NMR: 0.3 (OTMS), 26.6 (C6), 45.0 (C5a), 50.8 (C9a), 55.4 (C9-OCH$_3$), 56.5 (C4-OCH$_3$), 75.1 (C9), 101.6 (C3), 106.6 (C8), 122.8 (C4a), 127.7 (C3′ and C5′), 128.9 (C2′ and C6′), 130.4 (C4′), 138.1 (C1′), 153.1 (C7), 154.2 (C2), 162.1 (C10a), 165.4 (C4), 193.4 (C10), 196.3 (C5). *Anal.* Calcd for $C_{24}H_{27}NO_5Si$: C, 66.03; H, 6.00; N, 3.21. Found: C, 66.14; H, 6.26; N, 3.27.

Preparation of 7-Acetoxy-4-methoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (15b) A suspension of **14** (400 mg) in toluene (20 ml) was heated at 120 °C in the presence of small amount of silica gel in the sealed tube for 4 h. After removal of solvent *in vacuo*, the residue was treated with acetic anhydride–pyridine (2 : 1) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **15b** (308 mg, 90%) as yellow needles from $CHCl_3$, mp 233—234 °C. IR: 1765, 1686, 1663, 1599, 1578, 1535. UV: 235 (12000), 280 (30300). ^{1}H-NMR: 2.38 (3H, s, OCOCH$_3$), 4.19 (3H, s, OCH$_3$), 7.50—7.54 (3H, m, Ph), 7.51 (1H, dd, *J*=8, 2 Hz, 8-H), 7.57 (1H, s, 3-H), 7.95 (1H, d, *J*=2 Hz, 6-H), 8.16—8.18 (2H, m, Ph). 8.36 (1H, d, *J*=8 Hz, 9-H). ^{13}C-NMR: 21.1 (OCO<u>C</u>H$_3$), 56.8 (C4-OCH$_3$), 107.1 (C3), 118.7 (C4a), 120.0 (C8), 127.2 (C6), 127.8 (C3′ and C5′), 129.0 (C2′ and C6′), 129.4 (C9), 130.0 (C5a), 130.8 (C4′), 135.9 (C9a), 137.9 (C1′), 151.1 (C7), 155.6 (C2), 163.1 (C10a), 167.2 (C4), 168.6 (O<u>C</u>OCH$_3$), 180.9 (C10), 181.0 (C5). *Anal.* Calcd for $C_{22}H_{15}NO_5$: C, 70.77; H, 4.05; N, 3.75. Found: C, 70.54; H, 4.21; N, 3.79.

Preparation of 4,7-Dimethoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (15c) A solution of **15b** (200 mg) and conc. HCl (2 ml) in dioxane–water (3 : 1) (3 ml) was refluxed for 30 min. The reaction mixture was extracted with $CHCl_3$. The residue (169 mg) in THF (30 ml) was treated with excess CH_3I in the presence of KOH (297 mg, 8.8 mol eq) and TBAB (343 mg, 3.2 mol eq) at room temperature for 12 h under an Ar atmosphere. After removal of insoluble precipitates by filtration, the filtrate was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **15c** (138 mg, 75%) as yellow prisms from $CHCl_3$, mp 245—248 °C. IR: 1678, 1582, 1535. UV: 284 (33100). ^{1}H-NMR: 3.98 (3H, s, OCH$_3$), 4.18 (3H, s, OCH$_3$), 7.25 (1H, dd, *J*=9, 3 Hz, 8-H), 7.47—7.55 (4H, m, Ph and 3-H), 7.69 (1H, d, *J*=3 Hz, 6-H), 8.1—8.2 (2H, m, Ph), 8.28 (1H, d, *J*=9 Hz, 9-H). ^{13}C-NMR: 55.9 (C4-OCH$_3$), 56.6 (C7-OCH$_3$), 106.8 (C3), 110.0 (C8), 118.6 (C4a), 120.7 (C6), 126.1 (C5a), 127.7 (C3′ and C5′), 128.9 (C2′ and C6′), 129.8 (C9), 130.6 (C4′), 136.3 (C1′), 137.9 (C9a), 151.4 (C2), 162.9 (C7), 164.7 (C10a), 167.1 (C4), 180.7 (C10), 182.0 (C5). LRMS *m/z*: 345 (M^+). HRMS *m/z* (M^+): Calcd for $C_{21}H_{15}NO_4$: 345.1001. Found: 345.1016.

Preparation of (5*R,10*S**)-5,7,10-Triacetoxy-5,10-dihydro-4-methoxy-2-phenylbenzo[*g*]quinoline (16)** $NaBH_4$ (11 mg, 5 mol eq) was added to a solution of **15b** (60 mg) in EtOH (30 ml) at 0 °C and the mixture was stirred for 30 min at 0—25 °C. Water was added to the reaction mixture, which was then extracted with $CHCl_3$. The residue was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml). The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=5 : 1) to give **16** (54 mg, 73%) as a colorless gum. IR: 1738, 1589. UV: 277 (12000), 388 (500). ^{1}H-NMR: 2.00 (3H, s, 5-OCOCH$_3$), 2.31 (3H, s, 10-OCOCH$_3$), 2.41 (3H, s, 7-OCOCH$_3$), 4.01 (3H, s, OCH$_3$), 7.15 (1H, s, 10-H), 7.17 (1H, dd, *J*=9, 2 Hz, 8-H), 7.23 (1H, s, 3-H), 7.37 (1H, s, 5-H), 7.4—7.5 (4H, m, Ph and 6-H), 7.58 (1H, dd, *J*=9, 1 Hz, 9-H), 7.99—8.01 (2H, m, Ph). ^{13}C-NMR: 21.1 (C10-OCO<u>C</u>H$_3$), 21.2. (C5-OCO<u>C</u>H$_3$), 21.3 (C7-OCO<u>C</u>H$_3$), 55.9 (C4-OCH$_3$), 64.7 (C10), 68.7 (C5), 101.9 (C3), 114.9 (C4a), 122.3 (C8), 123.1 (C6), 126.6 (C9), 127.1 (C3′ and C5′), 128.7 (C2′ and C6′), 129.4 (C4′), 133.8 (C1′), 134.8 (C9a), 139.1 (C5a), 150.2 (C2), 157.1 (C7), 159.0 (C10a), 164.2 (C4), 169.3 (C10-O<u>C</u>OCH$_3$), 170.6 (C5-O<u>C</u>OCH$_3$), 171.2 (C7-O<u>C</u>OCH$_3$). LRMS *m/z*: 461 (M^+). HRMS *m/z* (M^+): Calcd for $C_{26}H_{23}NO_7$: 461.1472. Found: 461.1440.

Preparation of (5a*R,9*S**,9a*R**)-5a,8,9,9a-Tetrahydro-4,9-dimethoxy-2-phenylbenzo[*g*]quinoline-5,7,10(6*H*)-trione (17)** To a solution of **14** (200 mg) in THF (20 ml), 3 drops of 5% HCl–H_2O was added with stirring at room temperature for 5 min. The reaction mixture was extracted with $CHCl_3$. The residue was crystallized from MeOH to give **17** (126 mg, 75%) as yellow prisms, mp 190—192 °C. IR: 1717, 1638, 1578. UV: 166 (17700). ^{1}H-NMR: 2.42 (1H, dd, *J*=15, 7 Hz, 6-H), 2.52 (1H, dd, *J*=16, 3 Hz, 8-H), 2.92 (1H, dt, *J*=15, 3 Hz, 8-H), 3.03 (3H, s, 9-OCH$_3$), 3.41 (1H, dt, *J*=15, 2 Hz, 6-H), 3.62 (1H, dd, *J*=7, 3 Hz, 9a-H), 3.76 (1H, ddd, *J*=7, 2 Hz, 5a-H), 4.09 (3H, s, 4-OCH$_3$), 4.32 (1H, q, *J*=3 Hz, 9-H), 7.5—7.6 (4H, m, Ph and 3-H), 8.1—8.2 (2H, m, Ph). LRMS *m/z*: 365 (M^+). HRMS *m/z* (M^+): Calcd for $C_{21}H_{19}NO_5$: 365.1260. Found: 365.1258.

Preparation of 6,9-Dihydro-5,7,10-triacetoxy-4,9-dimethoxy-2-phenylbenzo[*g*]quinoline (20) Compound **17** (200 mg) was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was chromatographed over silica gel. Elution with $CHCl_3$ and crystallization from $CHCl_3$ gave **20** (48 mg, 18%) as yellow prisms, mp 224—225 °C. IR: 1765, 1671, 1580, 1560, 1510. UV: 242 (4000), 282 (9600), 331 (4800). ^{1}H-NMR: 2.22 (3H, s, 7-OCOCH$_3$), 2.39 (3H, s, 10-OCOCH$_3$), 2.55 (3H, s, 5-OCOCH$_3$), 2.70 (1H, dd, *J*=18, 2 Hz, 6-H), 3.04 (1H, ddd, *J*=18, 5, 2 Hz, 6-H), 3.31 (3H, s, 9-OCH$_3$), 4.03 (3H, s, 4-OCH$_3$), 4.85 (1H, dd, *J*=5, 2 Hz, 9-H), 6.56 (1H, d, *J*=2 Hz, 8-H), 7.20 (1H, s, 3-H), 7.4—7.5 (3H, m, Ph), 8.0—8.1 (2H, m, Ph). ^{13}C-NMR: 20.7 (C7-OCO<u>C</u>H$_3$), 21.0 (C10-OCO<u>C</u>H$_3$), 21.1 (C5-OCO<u>C</u>H$_3$), 32.8 (C6), 56.2 (C9-OCH$_3$), 56.3 (C4-OCH$_3$), 70.2 (C9), 100.1 (C3), 106.7 (C8), 115.5 (C4a), 123.0 (C5a), 124.4 (C9a), 127.3 (C3′ and C5′), 128.7 (C2′ and C6′), 129.6 (C4′), 138.4 (C1′), 139.3 (C7), 141.9 (C10), 144.0 (C5), 150.5 (C2), 157.7 (C10a), 168.4 (C4), 169.1 (C7-O<u>C</u>OCH$_3$), 169.4 (C5 and C10-O<u>C</u>OCH$_3$). LRMS *m/z*: 491 (M^+). HRMS *m/z* (M^+): Calcd for $C_{27}H_{25}NO_8$: 491.1581. Found: 491.1591.

Preparation of (5*R,5a*R**,7*S**,9*S**,9a*R**,10*S**)-5,7,10-Triacetoxy-5,5a,6,7,8,9,9a,10-octahydro-4,9-dimethoxy-2-phenylbenzo[*g*]quinoline (19a)** $NaBH_4$ (52 mg, 5 mol eq) was added to a solution of **17** (100 mg) in MeOH (20 ml) at 0 °C and the mixture stirred for 1 h at room temperature. Water was added to the reaction mixture, which was then extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **18** (101 mg, 100%) as colorless prisms from $CHCl_3$–Et_2O, mp 142—153 °C. IR: 3368, 1591, 1542. UV: 390 (600), 260 (12700). ^{1}H-NMR: 2.2—2.5 (5H, m), 3.24 (3H, s), 4.0—4.2 (5H, m), 4.7—4.9 (3H, m), 7.17 (1H, s), 7.4—7.6 (3H, m), 8.0—8.1 (2H, m). LRMS *m/z*: 371 (M^+). HRMS *m/z* (M^+): Calcd for $C_{21}H_{25}NO_5$: 371.1733. Found: 371.1754.

Compound **18** (100 mg) was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was then crystallized from $CHCl_3$ to give a 3 : 1 mixture of **19a** and **19b** (86 mg, 64%) as colorless prisms, mp 145—173 °C. Repeated recrystallization of the mixture from $CHCl_3$ gave **19a** as colorless prisms, mp 175—177 °C. IR: 1734, 1597, 1562. UV: 264 (3900). ^{1}H-NMR: 1.8—1.9 (2H, m, 6-H×2), 2.05 (3H, s, 7-OCOCH$_3$), 2.144 (6H, s, 5-OCOCH$_3$ and 10-OCOCH$_3$), 2.3—2.4 (2H, m, 8-H×2), 2.4—2.5 (1H, m, 5a-H), 2.6—2.7 (1H, m, 9a-H), 3.41 (3H, s, 9-OCH$_3$), 3.51—3.54 (1H, m, 7-H), 3.93 (3H, s, 4-OCH$_3$), 4.8—4.9 (1H, m, 9-H), 6.39—6.41 (2H, m, 5-H and 10-H), 7.19 (1H, s, 3-H), 7.4—7.5 (3H, m, Ph), 7.99—8.02 (2H, m, Ph). ^{13}C-NMR: 20.8 (OCO<u>C</u>H$_3$), 21.4 (OCO<u>C</u>H$_3$), 22.0 (OCO<u>C</u>H$_3$), 27.3 (C6), 32.6 (C5a), 34.2 (C8), 35.9 (C9a), 55.7 (C9-OCH$_3$), 56.9 (C4-OCH$_3$), 67.0 (C10), 67.3 (C5), 70.8 (C7), 77.6 (C9), 102.2 (C3), 116.7 (C4a), 126.9 (C3′ and C5′), 128.7 (C27 and C6′), 129.4 (C4′), 138.6 (C1′), 154.7 (C2), 158.7 (C10a), 165.6 (C4), 169.0 (O<u>C</u>OCH$_3$), 170.3 (O<u>C</u>OCH$_3$), 170.5 (O<u>C</u>OCH$_3$).

Anal. Calcd for $C_{27}H_{31}NO_8$: C, 65.18; H, 6.28; N, 2.82. Found: C, 65.46; H, 6.37; N, 2.77.

^{1}H- and ^{13}C-NMR Data for (5*R,5a*R**,7*R**,9*S**,9a*R**,10*S**)-5,7,10-Triacetoxy-5,5a,6,7,8,9,9a,10-octahydro-4,9-dimethoxy-2-phenylbenzo[*g*]quinoline (19b)** Data for **19b** were obtained from the spectra of the mixture (**19a** and **19b**). ^{1}H-NMR: 1.9—2.0 (2H, m, 6-H×2), 2.03 (3H, s, 7-OCOCH$_3$), 2.141 (6H, s, 5-OCOCH$_3$ and 10-OCOCH$_3$), 2.3—2.4 (2H, m, 8-H×2), 2.4—2.5 (1H, m, 5a-H), 2.6—2.7 (1H, m, 9a-H), 3.47 (3H, s, 9-OCH$_3$), 3.56—3.59 (1H, m, 7-H), 3.93 (3H, s, 4-OCH$_3$), 4.99—5.01 (1H, m, 9-H), 6.42—6.46 (2H, m, 5-H and 10-H), 7.14 (1H, s, 3-H), 7.4—7.5 (3H, m, Ph), 7.99—8.02 (2H, m, Ph). ^{13}C-NMR: 20.7 (OCO<u>C</u>H$_3$), 21.4 (OCO<u>C</u>H$_3$), 22.0 (OCO<u>C</u>H$_3$), 27.2 (C6), 32.6 (C5a), 33.3 (C8), 36.5 (C9a), 55.7 (C9-OCH$_3$), 56.8 (C4-OCH$_3$), 67.0 (C10), 67.3 (C5), 71.1 (C7), 78.5 (C9), 102.2 (C3), 116.7 (C4a), 126.9 (C3′ and C5′), 128.7 (C27 and C6′), 129.3 (C4′), 138.6 (C1′), 154.7 (C2), 158.7 (C10a), 165.6 (C4), 169.0 (O<u>C</u>OCH$_3$), 169.9 (O<u>C</u>OCH$_3$), 170.7 (O<u>C</u>OCH$_3$).

Preparation of (5a*R,9*S**,9a*R**,10*S**)-10-Acetoxy-5a,6,8,9,9a,10-hexahydro-4,9-dimethoxy-2-phenylbenzo[*g*]quinoline-5,7-dione (21)** $LiBH_4$ (10 mg, 0.5 mol eq) was added to a solution of **14** (100 mg) in THF (20 ml) at −60 °C and the mixture was stirred for 1 h at the same temperature. After decomposition of excess hydride with water, the mixture was extracted with $CHCl_3$. The residue was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 13 h. The reaction mixture was extracted with $CHCl_3$. The residue was crystallized from $CHCl_3$–Et_2O to give **21** (40 mg, 40%) as colorless prisms, mp 239—242 °C. IR: 1715, 1686. UV: 285 (9800). ^{1}H-NMR: 2.35 (3H, s, 10-OCOCH$_3$), 2.39 (1H, dd, *J*=15, 3 Hz, 8*β*-H), 2.42 (1H, dd, *J*=15, 7 Hz, 6*α*-H), 2.82 (1H, dt, *J*=15, 3 Hz, 8*α*-H), 2.98 (3H, s, OCH$_3$), 3.16 (1H, ddd, *J*=7, 5, 2 Hz, 9a-H), 3.34 (1H ddd, *J*=7, 5, 2 Hz, 5a-H), 3.47 (1H, dt, *J*=15, 2 Hz, 6*β*-H), 4.03 (3H, s, OCH$_3$), 4.18 (1H, dd, *J*=5, 3 Hz, 9*β*-H), 6.61 (1H, d, *J*=7 Hz, 10*β*-H), 7.23 (1H, s, 3-H), 7.4—7.5 (3H, m, Ph), 8.01—8.04 (2H, m, Ph). ^{13}C-NMR: 21.3 (OCO<u>C</u>H$_3$), 39.4 (C6), 43.7 (C9a), 44.4 (C8), 46.2 (C5a), 56.1 (C4-OCH$_3$), 56.6 (C9-OCH$_3$), 69.9 (C10), 76.3 (C9), 102.5 (C3), 116.6 (C4a), 127.3 (C3′ and C5′), 128.8 (C2′ and C6′), 130.2 (C4′), 138.3 (C1′), 160.4 (C10a), 160.7 (C2), 165.8 (C4), 170.8 (O<u>C</u>OCH$_3$), 192.5 (C5), 205.9 (C7). LRMS *m/z*: 409 (M^+). *Anal.* Calcd for $C_{23}H_{23}NO_8$: C, 67.47; H, 5.66; N, 3.42. Found: C, 65.04; H, 5.68; N, 3.30.

Diels–Alder Reaction of 10a with 1-Methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene A solution of **10a** (200 mg) and 1-methoxy-1,3-bis-(trimethylsilyloxy)-1,3-butadiene (607 mg, 3 mol eq) in benzene (5 ml) was stirred at room temperature for 5 min in a sealed tube under an Ar atmosphere. After removal of the solvent *in vacuo*, the residue in THF (20 ml) was treated with 3 drops of 5% HCl–H_2O at room temperature for 5 min. The reaction mixture was extracted with $CHCl_3$. The residue was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **24** (31 mg, 10%) and **23a** (106 mg, 31%).

4,8-Diacetoxy-6-methoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (**23a**): Yellow prisms from $CHCl_3$–Et_2O, mp 245—253 °C. IR: 1775, 1696, 1665, 1595, 1543. UV: 271 (15100), 376 (4300). ^{1}H-NMR: 2.38 (3H, s, OCOCH$_3$), 2.55 (3H, s, OCOCH$_3$), 4.02 (3H, s, OCH$_3$), 7.15 (1H, d, *J*=2 Hz, 9-H), 7.5—7.6 (3H, m, Ph), 7.72 (1H, d, *J*=2 Hz, 7-H), 7.74 (1H, s, 3-H), 8.1—8.2 (2H, m, Ph). ^{13}C-NMR: 21.2 (OCO<u>C</u>H$_3$), 21.3 (OCO<u>C</u>H$_3$), 57.0 (OCH$_3$), 112.0 (C3), 119.6 (C4), 119.8 (C9), 122.7 (C9a), 127.7 (C3′ and C5′), 129.0 (C2′ and C6′), 131.0 (C4′), 136.2 (C4a), 136.8 (C1′), 149.9 (C8), 155.7 (C2), 158.4 (C4), 161.8 (C6), 162.9 (C10a), 168.4 (O<u>C</u>OCH$_3$), 168.6 (O<u>C</u>OCH$_3$), 179.9 (C10), 180.8 (C5). LRMS *m/z*: 431 (M^+). *Anal.* Calcd for $C_{24}H_{17}NO_7$: C, 66.82; H, 3.97; N, 3.25. Found: C, 66.79; H, 3.99; N, 3.14.

4,5,8-Triacetoxy-2-phenylquinoline (**24**): Yellow prisms from $CHCl_3$–Et_2O, mp 63—64 °C. IR: 1765, 1603, 1562, 1510. UV: 268 (28000). ^{1}H-NMR: 2.41 (3H, s, OCOCH$_3$), 2.44 (3H, s, OCOCH$_3$), 2.53 (3H, s, OCOCH$_3$), 7.15 (1H, d, *J*=8 Hz, 6-H), 7.4—7.6 (3H, m, Ph), 7.45 (1H, d, *J*=8 Hz, 7-H), 7.65 (1H, s, 3-H), 8.0—8.1 (2H, m, Ph). ^{13}C-NMR: 20.9 (OCO<u>C</u>H$_3$), 21.1 (OCO<u>C</u>H$_3$), 21.2 (OCO<u>C</u>H$_3$), 113.5 (C3), 116.9 (C4a), 119.8 (C6), 121.3 (C7), 127.5 (C3′ and C5′), 128.8 (C2′ and C6′), 130.1 (C4′), 138.1 (C1′), 142.3 (C8), 143.5 (C5), 146.1 (C4), 153.8 (C2), 158.0 (C8a), 167.9 (O<u>C</u>OCH$_3$), 169.1 (O<u>C</u>OCH$_3$), 169.5 (O<u>C</u>OCH$_3$). *Anal.* Calcd for $C_{21}H_{17}NO_6$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.47; H, 4.60; N, 3.42.

Preparation of 24 A solution of $Na_2S_2O_4$ (1.3 g, 20 mol eq) in H_2O (3 ml) was added to a solution of **10a** (100 mg) in dioxane–H_2O (1 : 1) (10 ml) at 0 °C and the mixture was stirred for 15 min. Crystalline precipitates were collected by filtration and washed with H_2O and Et_2O. This material was then treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was crystallized from $CHCl_3$–Et_2O to give **24** (70 mg, 73%).

Preparation of 4,6,7-Trimethoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (23b) A solution of **23a** (10 mg) and conc. HCl (2 ml) in dioxane–H_2O (3 : 1) (3 ml) was refluxed for 1 h. The reaction mixture was extracted with $CHCl_3$. The residue in DMF (2 ml) was treated with excess CH_3I in the presence of K_2CO_3 (7 mg, 3 mol eq) at room temperature for 37 h. After removal of insoluble precipitates by filtration, the filtrate was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) to give **23b** (7 mg, 80%) as yellow needles from $CHCl_3$–Et_2O, mp 250—253 °C. IR: 1688, 1651, 1603. UV: 225 (16700), 283 (27900), 386 (4500). ^{1}H-NMR: 3.98 (3H, s, OCH$_3$), 3.99 (3H, s, OCH$_3$), 4.14 (3H, s, OCH$_3$), 6.80 (1H, d, *J*=2 Hz, 7-H), 7.42 (1H, d, *J*=2 Hz, 9-H), 7.5—7.6 (4H, m, Ph and 3-H), 8.1—8.2 (2H, m, Ph), LRMS *m/z*: 375 (M^+). HRMS *m/z* (M^+): Calcd for $C_{22}H_{17}NO_5$: 375.1104. Found: 375.1093.

Diels–Alder Reaction of 10b with 1-Methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene A solution of **10b** (200 mg) and 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (575 mg, 3 mol eq) in benzene (5 ml) was stirred at room temperature for 30 min in a sealed tube under an Ar atmosphere. After removal of the solvent *in vacuo*, the residue in THF (20 ml) was treated with 3 drops of 5% HCl–H_2O at room temperature for 5 min. The reaction mixture was extracted with $CHCl_3$. The residue was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=4 : 1) to give **27** (26 mg, 10%). Futher elution with hexane–AcOEt (1 : 1) gave **26a** (78 mg, 33%).

Compound **26a** in THF (10 ml) was treated with excess CH_3I, KOH (124 mg, 8.8 mol eq) and TBAB (51 mg, 1.2 mol eq.) for 43 h at room temperature under an Ar atmosphere. After removal of insoluble materials by filtration, the filtrate was extracted with $CHCl_3$. The residue was purified by column chromatography (hexane : AcOEt=1 : 1) to give **26b** (74 mg, 26% from **10b**).

4,7,9-Trimethoxy-2-phenylbenzo[*g*]quinoline-5,10-dione (**26b**): Yellow prisms from $CHCl_3$–Et_2O, mp 235—237 °C. IR: 1671, 1584, 1537. UV: 286 (23700), 345 (7300). ^{1}H-NMR: 3.97 (3H, s, OCH$_3$), 4.00 (3H, s, OCH$_3$), 4.17 (3H, s, OCH$_3$), 6.76 (1H, d, *J*=2 Hz, 8-H), 7.39 (1H, d, *J*=2 Hz, 6-H), 7.4—7.6 (4H, m, Ph and 3-H), 8.1—8.3 (2H, m, Ph). ^{13}C-NMR: 55.9 (OCH$_3$), 56.56 (OCH$_3$), 56.61 (OCH$_3$), 103.1 (C8), 104.2 (C6), 105.9 (C3), 115.8 (C4a), 117.3 (C9a), 127.7 (C3′ and C5′), 128.9 (C2′ and C6′), 130.6 (C4′), 138.0 (C1′), 138.4 (C5a), 152.8 (C2), 162.3 (C10a), 163.0 (C7), 165.0 (C9), 166.6 (C4), 179.7 (C10), 182.4 (C5). LRMS *m/z*: 375 (M^+). HRMS *m/z* (M^+): Calcd for $C_{22}H_{17}NO_5$: 375.1108. Found: 375.1141.

5,8-Diacetoxy-4-methoxy-2-phenylquinoline (**27**): Yellow prisms from $CHCl_3$–Et_2O, mp 167—168 °C. IR: 1769, 1754, 1702, 1686, 1655, 1649. UV: 262 (34100), 300 (8000). ^{1}H-NMR: 2.37 (3H, s, OCOCH$_3$), 2.52 (3H, s, OCOCH$_3$), 4.05 (3H, s, OCH$_3$), 7.06 (1H, d, *J*=8 Hz, 6-H), 7.22 (1H, s, 3-H), 7.39 (1H, d, *J*=8 Hz, 7-H), 7.4—8.1 (5H, m, Ph). ^{13}C-NMR: 20.9 (OCO<u>C</u>H$_3$), 21.0 (OCO<u>C</u>H$_3$), 56.2 (OCO<u>C</u>H$_3$), 99.6 (C3), 115.5 (C4a), 118.5 (C7), 121.2 (C6), 127.5 (C3′ and C5′), 128.7 (C2′ and C6′), 129.8 (C4′), 139.4 (C1′), 143.2 (C8), 143.7 (C5), 145.8 (C2), 158.5 (C10a), 163.0 (C4), 169.8 (O<u>C</u>OCH$_3$), 170.0 (O<u>C</u>OCH$_3$). LRMS *m/z*: 351 (M^+). HRMS *m/z* (M^+): Calcd for $C_{20}H_{17}NO_5$: 351.1105. Found: 351.1090.

Preparation of 27 A solution of $Na_2S_2O_4$ (1.3 g, 20 mol eq) in H_2O (3 ml) was added to a suspension of **10b** (100 mg) in dioxane–H_2O (1 : 1) (10 ml) at 0 °C and the mixture was stirred for 15 min. Crystalline precipitates were collected by filtration and then washed with H_2O and Et_2O. This material was treated with acetic anhydride–pyridine (1 : 2) (1.5 ml) at room temperature for 15 h. The reaction mixture was extracted with $CHCl_3$. The residue was purified by column chromatography ($CHCl_3$) and crystallization from $CHCl_3$–Et_2O to give **27** (86 mg, 70%).

References and Notes

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8) The formation of the hydroquinone may be explained by an oxidation–reduction reaction between the quinone **10a** and the Diels–Alder adduct **22**.
9) The product **26a** was not acetylated because of the extreme insolubility in pyridine.