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Reactivity of Nitrovinylquinones with Cyclic and Acyclic Enol Ethers

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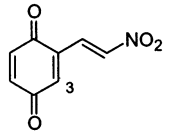
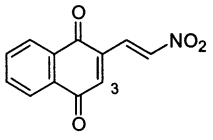
The nitrovinyl-substituted quinones 2-(2-nitrovinyl)-1,4-benzoquinone and 2-(2-nitrovinyl)-1,4-naphthoquinone react with a variety of cyclic and acyclic enol ethers via two competing pathways. In one pathway, the nitrovinylquinone acts as an inverse electron-demand [4 + 2] diene. This gives quinoid carbocycles, which readily tautomerize to their hydroquinone form. The other pathway involves conjugate (Michael) addition of the enol ether to the nitrovinylquinone, followed by ring closure. This gave dihydrobenzofurans, which can eliminate an alcohol to give benzofurans. Hindered enol ethers tended to favor the conjugate addition pathway, while less hindered enol ethers favored cycloaddition.

Introduction

Nitrovinyl-substituted quinones are an unusual class of reactive, very electron-deficient molecules. Two simple nitrovinylquinones, 2-(2-nitrovinyl)-1,4-benzoquinone (**1a**) and 2-(2-nitrovinyl)-1,4-naphthoquinone (**1b**), are shown below.



1a

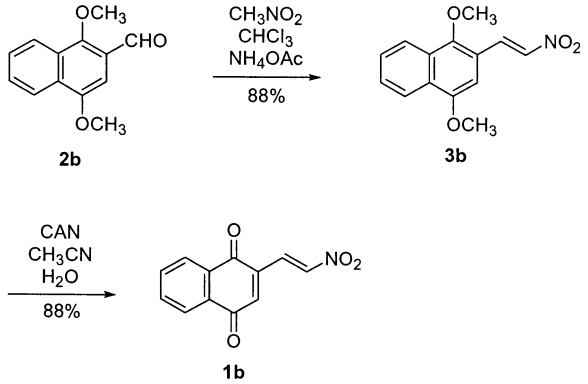


1b

Multiple sites and modes are available for the reaction of nitrovinylquinones **1a** and **1b** with electron-rich unsaturated molecules. Nitrovinylquinones can react in inverse electron-demand [4 + 2] cycloadditions as electron-poor carbon dienes. They are also good Michael acceptors in conjugate addition reactions, as well as being oxidizing agents. Despite the potentially bewildering array of possible products, it was found previously that **1a** reacted with electron-rich unsaturated heterocycles with good selectivity for a narrow range of products.[1] With aromatic heterocycles, such as furans and indoles, **1a** was highly selective as a diene for [4 + 2] cycloaddition. With nonaromatic, enol ether-like heterocycles, such as dihydrofuran and 3,4-dihydro-2*H*-pyran, however, a mixture of conjugate addition and cycloaddition products was observed, generally favoring the former.

In continuation of the study of nitrovinylquinones, this paper details the reactivity of **1a** and **1b** with a variety of cyclic and acyclic enol ethers. The goals of this work included extending the scope and utility of nitrovinylquinones in synthesis, as well as comparing and contrasting the reactivity of nitrovinylquinones with heterocycles with that of enol ethers to establish more general reactivity trends for these molecules.

SCHEME 1



Results and Discussion

The synthesis of nitrovinylquinones **1a** and **1b** was accomplished in two steps from 1,4-dimethoxyaryl-2-aldehydes. The synthesis of **1a** from 2,5-dimethoxybenzaldehyde has been reported previously by us.[1] The synthesis of **1b** is described in Scheme 1.

Naphthalenecarboxaldehyde **2b** was prepared from naphthoquinone according to literature methods.[2,3] The aldehyde **2b** was converted to the β-nitrostyrene analogue **3b** by reaction with nitromethane and ammonium acetate.[4] The nitrovinylquinone **1b** was then formed by

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(1) Noland, W. E.; Kedrowski, B. L. *J. Org. Chem.* **1999**, *64*, 596−603.

(2) Smith, L. I.; Wawzonek, S.; Miller, H. *J. Org. Chem.* **1941**, *6*, 229−232.

(3) Syper, L.; Mlochowski, J.; Kloc, K. *Tetrahedron* **1983**, *39*, 781−792.

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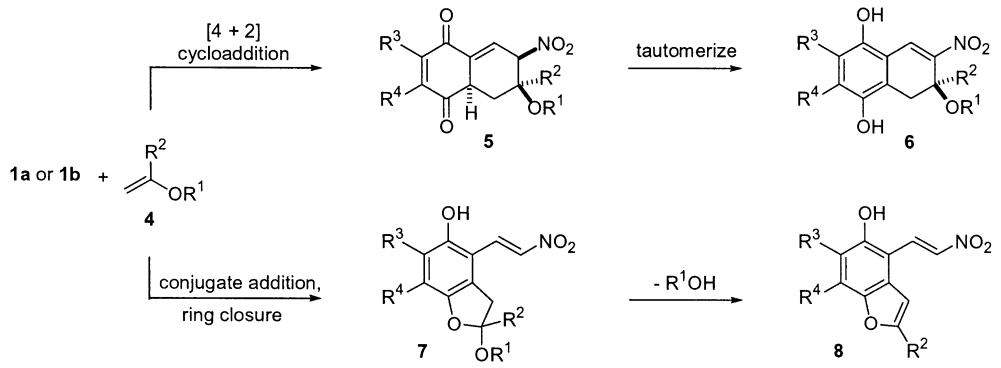
TABLE 1. Reactions of 1a and 1b with Acyclic Enol Ethers



entry	R^1	R^2	R^3, R^4	solvent	product(s)	ratio	yield,[a] %
1	Me	H	H, H	THF	**6a**		47
2	Et	H	H, H	neat	**6b**		53
3	Et	H	H, H	PhH	**6b**		44
4	*t*-Bu	H	H, H	THF	**6c, 7c**	2.3:1	53
5	Me	Me	H, H	THF	**7d**		33
6	Me	Me	H, H	THF[b]	**8d**		53
7	Et	H	−CH=CHCH=CH−	neat	**6e**		42
8	Et	H	−CH=CHCH=CH−	THF	**5e**		87

[a] Isolated yield. [b] The crude reaction mixture was treated with TsOH in PhH prior to workup.

oxidative demethylation of **3b** with ceric ammonium nitrate (CAN).[5]

Reactions with Acyclic Enol Ethers. Several readily available alkyl enol ethers (**4**) were examined in reactions with **1a** and **1b** (Table 1). Three solvents were utilized for these reactions: benzene, THF, and the neat enol ether. In the cases examined with acyclic enol ethers, all of these solvents gave similar results.

Four major products are generally observed, resulting from two competing pathways. The first pathway, inverse electron-demand [4 + 2] cycloaddition, gives products of type **5**. The reactions are highly regioselective, giving only a single detectable regioisomer in each case. Carbon C3 of **1a** and **1b** is the most electrophilic, due to simultaneous conjugation with nitro and carbonyl groups, leading to the observed regioselectivity. Compounds **5** are highly prone to tautomerization and aromatization, and readily convert to **6**, so often it was not possible to isolate **5**. In entry 8 (Table 1) compound **5e** was isolated from the reaction before it tautomerized. The stereochemistry of this cycloadduct was determined to be *exo* by ^{1}H NMR coupling constant analysis.

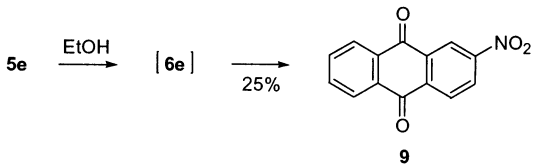
The second pathway likely involves conjugate addition of the alkyl enol ether to the quinone, followed by an intramolecular ring closure to compounds of type **7**. Analogous behavior of related quinones has been reported with electronically similar species such as silyl enol ethers,[6] as well as other electron-rich unsaturated substrates.[7a,b] Compounds **7** can eliminate R^1OH to give benzofurans **8**, and it is sometimes difficult to isolate **7**. This elimination is promoted by acid, which can be used to efficiently convert **7** to **8** and thereby simplify the product mixture.

(5) Jacob, P.; Callery, P. S.; Shulgin, A. T.; Castagnoli, N. *J. Org. Chem.* **1976**, *41*, 3627−3629.

(6) Mukaiyama, T.; Sagawa, Y.; Kobayashi, S. *Chem. Lett.* **1987**, 2169−2172.

(7) (a) Titov, E. A.; Grishchenko, A. S. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1972**, *8*, 789−791. (b) Engler, T. A.; Iyengar, R. *J. Org. Chem.* **1998**, *63*, 1929−1934 and references therein.

SCHEME 2

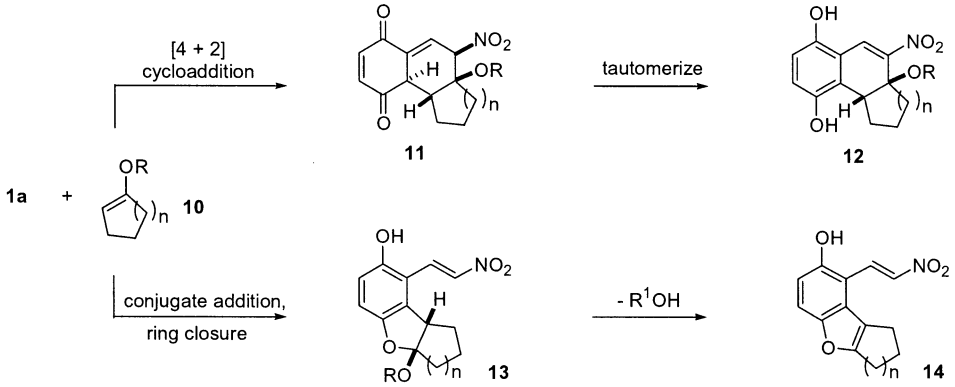


Steric hindrance appears to be a significant factor in determining which products are formed. With sterically unencumbered alkyl enol ethers such as methyl vinyl ether and ethyl vinyl ether (entries 1−3, 7, and 8), the cycloaddition pathway was strongly preferred and no other products were isolated. The bulkier *tert*-butyl vinyl ether (entry 4) gave a mixture of cycloaddition and conjugate addition products, and methyl 2-propenyl ether (entries 5 and 6) gave only conjugate addition products as the isolated products.

Compound **6e** was somewhat unstable and had a tendency to eliminate ethanol and autoxidize to form 2-nitroanthraquinone (**9**), Scheme 2. This was discovered in an attempt to recrystallize **6e** in hot ethanol. It was later observed that this reaction also occurs in ethanol solution at room temperature. Compound **5e** could be converted directly to **9** in an unoptimized overall yield of 25% from **1b** by heating in ethanol (Scheme 2).

Reactions with Cyclic Enol Ethers. Several readily available cyclic enol ethers (**10**) were examined in reactions with **1a** (Table 2). Nitrovinylquinone **1b** yielded only intractable mixtures with these cyclic enol ethers. The reactivity patterns for **1a** with cyclic enol ethers generally followed those with acyclic enol ethers, but there are some notable differences. Four major products were again observed, resulting from [4 + 2] cycloaddition and conjugate addition/ring closure pathways. In contrast to previous results with acyclic enol ethers, in these examples, solvent choice was significant. The use of benzene often caused one product to precipitate out selectively,

TABLE 2. Reactions of 1a with Cyclic Enol Ethers



entry	R	n	solvent	product(s)	mole ratio	combined yield,[a] %
1	Me	1	PhH	**11a, 13a**	1:6.8	39
2	Me	1	PhH	**12a,**[b] **13a**	1:2.1	66
3	Me	2	PhH	**11b**[c]		22
4	Et	2	PhH	**11c, 13c**	1.2:1	44
5	TMS	2	PhH	**14d**		55
6	TMS	2	THF[d]	**14d**		40
7	Me	3	PhH	**11e, 13e**	1:2.4	71
8	Me	3	THF[e]	**11e, 14e**	1:4.7	51

[a] Isolated yields. [b] Et_3N was added to tautomerize **11a** to **12a** prior to workup. [c] Conjugate addition products were not isolated. [d] The crude reaction mixture was treated with HCl in MeOH prior to workup. [e] The crude reaction mixture was treated with TsOH in PhH prior to workup.

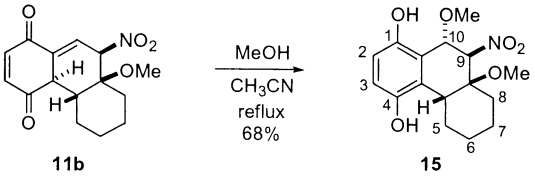
and in this way the initial cycloaddition products **11** could often be isolated.

In reactions of **1a** with cyclic enol ethers, the conjugate addition/cyclization pathway is more prevalent than with acyclic enol ethers. This is likely related to the inherently greater steric bulk of cyclic enol ethers relative to acyclic enol ethers. With cyclic enol ethers, the conjugate addition/cyclization pathway is generally the preferred pathway, often by a large margin. In entries 1 and 2 ($n = 1$), conjugate addition products dominated. In entry 1, conjugate addition/cyclization product **13a** was isolated along with the cycloaddition product **11a**. The low yield of **11a** reflects the difficulty of isolation of this compound. In entry 2 the crude reaction mixture was treated with Et_3N to convert **11a** to **12a** to simplify isolation. Compound **12a** was much easier to isolate, giving a better yield of the product from the cycloaddition pathway. With the exception of **13a** ($n = 1$), products of type **13** were prone to eliminate alcohol to give benzofurans **14**. Compound **13a** is particularly resistant to this elimination, perhaps due to the extra ring strain associated with having a double bond between two five-membered rings. With other ring sizes, it was difficult to isolate and/or purify **13,** as these efforts promoted conversion of **13** to **14**. This was observed in entry 3, where the cycloaddition product **11b** was produced along with conjugate addition products that were not isolated. In entry 4, cycloaddition product **11c** was produced along with **13c**. In this case, **13c** could be purified somewhat by chromatography, giving a 3.9:1 ratio of **13c** to **14c**. This mixture could be purified further by recrystallization to give pure **13c** as indicated in Table 2. In entries 5 and 6 reactions of **1a** with the very bulky 1-trimethylsiloxycyclohexene led to the conjugate addition/cyclization product **14d** as the only product isolated. In entry 5, the benzofuran **14d** was produced directly. In entry 6, in THF **13d** was prone to elimination to form **14d**. In this case, workup and purification were simplified by treatment with HCl/MeOH to convert the intermediate silyl ether to **14d**. In entry 7, a mixture of cycloaddition product **11e** and conjugate addition product **13e** was produced. In this case, it was possible to isolate and purify **13e**. Entry 8 was similar to entry 7, except the reaction was carried out in THF, leading to **13e** and a lower yield of **11e**. In this case, **13e** was converted to **14e** in situ by treatment with acid prior to workup.

The regiochemistry of [4 + 2] cycloadducts **11** follows that observed with acyclic enol ethers. These reactions are *exo* with respect to the ring of the enol ether (*endo* with respect to the alkoxy substituent). This was determined by ^1H NMR coupling constant analysis when possible. Due to the labile nature of tautomer **11** in polar solvents, only less polar NMR solvents such as $CDCl_3$ or benzene-d_6 could be used with these molecules. The solubility of **11** in these solvents was somewhat low, making carbon NMR spectra difficult to obtain. Proton NMR data for **11** gave acceptable spectra when $n = 1$ or 3, but not when $n = 2$, where the peaks were severely broadened. The situation was improved somewhat by obtaining ^1H NMR spectra at elevated temperatures (50 °C) in benzene, but many coupling constants were still not resolved.

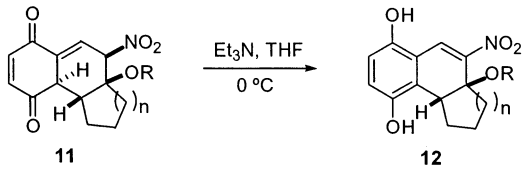
To determine the relative stereochemistry of **11b**, and to verify the assignment in other compounds of type **11**, single-crystal X-ray analysis of **11b** was obtained. The data showed that the reaction between **1a** and 1-methoxycyclohexene gave **11b** with *exo* selectivity with respect to the cyclohexene ring. It is likely that reaction of **1a** with 1-ethoxycyclohexene to form **11c** proceeded similarly, giving an *exo* product. Selectivity for an *exo* transition state in cycloaddition reactions with enol ethers is a departure from that observed previously for aromatic furan heterocycles, which yield *endo* products with **1a**.[1] With aromatic heterocycles, there is opportunity

SCHEME 3



11b 15

TABLE 3. Tautomerization of 11 to 12



11 12

reactant	R	n	product	yield, %
11b	Me	2	**12b**	74
11c	Et	2	**12c**	69
11e	Me	3	**12e**	70

for secondary orbital overlap that can stabilize an *endo* transition state. With enol ethers, no such stabilization exists and *exo* approach is probably favored for steric reasons.

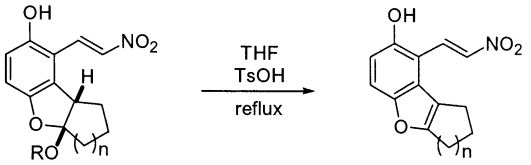
In an interesting side reaction, it was found that **11b** reacts with methanol in a conjugate addition reaction to produce the dimethoxy derivative **15** (Scheme 3). Careful choice of conditions was important in this reaction since tautomerization occurs competitively with addition of methanol. The relative stereochemistry of the newly added methoxyl group was found to be *trans* to the nitro group. The proton−proton coupling constant between C9−H and C10−H was large, 8.5 Hz, suggesting a pseudoaxial relationship between the two protons. Although this was the only case in which addition of a nucleophile to **13** was attempted, it may be possible to add others. This could lead to other, more highly substituted carbocycles such as **15**.

Conversion of 11 to 12. As described above, compounds of type **11** tautomerize readily to **12**. This transformation can be effected in good yield by reaction of **11** with catalytic Et_3N in THF at 0 °C. These data are summarized in Table 3.

Tautomerization of pure **11a** was not attempted because this starting material was rather difficult to obtain in quantity, and because its in situ tautomerization to **12a** by Et_3N had been demonstrated previously in Table 2.

Conversion of 13 to 14. Compounds of type **13** could often be converted to **14** by acid-catalyzed elimination of ROH. These data are summarized in Table 4. In the first example, **13a** was resistant to elimination and failed to yield detectable quantities of **14a** after 24 h of refluxing in THF with 30 mol % TsOH. Under forcing conditions, with acid in refluxing toluene for 17 h, some elimination product was detected by ^{1}H NMR, but a significant amount of decomposition had occurred, and starting material remained. In the second example, elimination of ethanol was rapid, forming **14c** within 1 h in refluxing THF with 10 mol % TsOH. In the third example ($n = 3$), the reaction was slower and required 15 h in refluxing THF with 30 mol % TsOH.

TABLE 4. Acid-Catalyzed Conversion of 13 to 14



13 14

reactant	R	n	product	yield, %
13a	Me	1		no reaction
13c	Et	2	**14c**[a]	90
13e	Me	3	**14e**	88

[a] Compound **14c** is the same as **14d** ($n = 2$) from Table 2.

Conclusions

It was found that nitrovinylquinones such as **1a** and **1b** can serve as useful precursors in the formation of carbocyclic and benzofuran rings. The reactivity of nitrovinylquinones with enol ethers is similar in some respects to that observed previously in reactions with aromatic heterocycles.[1] The major difference in reactivity between enol ethers and heterocycles is a preference for a conjugate addition/cyclization pathway to form benzofurans over the cycloaddition pathway, which leads to carbocycles. Both steric and electronic factors are likely responsible for this shift in selectivity.

Experimental Section

General Methods. Benzene, toluene, and CH_2Cl_2 were dried by distillation from CaH_2; tetrahydrofuran (THF) was dried by distillation from sodium/benzophenone. Reagents were purchased and used as received, unless otherwise noted. Brine refers to saturated aqueous NaCl solution. Reactions were monitored by TLC on precoated silica gel plates. Flash chromatography was performed with silica gel 60, 230−400 mesh. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, unless otherwise noted. Carbon NMR spectra were acquired proton decoupled. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ. Cyclic enol ethers **10** were prepared from the corresponding cyclic ketones by literature methods.[8]

1,4-Dimethoxy-2-(2-nitrovinyl)naphthalene (3b). A mixture of aldehyde **2b** (30.23 g, 139.8 mmol), CH_3NO_2 (95 mL), $CHCl_3$ (233 mL), and ammonium acetate (2.69 g, 35.0 mmol) was heated at reflux. After 5 days of refluxing, an additional portion of ammonium acetate (2.69 g, 35.0 mmol) was added and refluxing was resumed for 24 h. The reaction mixture was cooled to room temperature, and volatile components were removed under vacuum. The resulting orange residue was crystallized from *i*-PrOH/H_2O, giving **3b** as orange crystals (30.85 g, 88%): mp 147−148 °C; all spectral data (IR, ^{1}H NMR, ^{13}C NMR, HRMS) agree with the published data.[4] Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.53; H, 4.97; N, 5.06.

2-(2-Nitrovinyl)-1,4-naphthoquinone (1b). A solution of ceric ammonium nitrate (23.28 g, 42.5 mmol) in CH_3CN (30 mL) and H_2O (30 mL) was poured into a solution of compound **3b** (5.00 g, 19.3 mmol) in CH_3CN (250 mL), with rapid stirring. The color changed rapidly from orange to black to red. After 10 min, brine (50 mL) was added and the resulting phases were separated. The aqueous phase was extracted with CH_3CN, and the combined CH_3CN extracts were evaporated under vacuum. The resulting residue was extracted with $CHCl_3$ (2

(8) Wohl, R. A. *Synthesis* **1974**, 38−40.

× 120 mL) and filtered. The combined $CHCl_3$ fractions were washed with H_2O (3 × 50 mL), dried over $MgSO_4$, and filtered, and the solvent was evaporated under vacuum, giving a brown solid. Crystallization from CH_2Cl_2/cyclohexane gave **1b** as brown-red crystals. The filtrate was evaporated and the residue recrystallized, producing additional pure crystals (total 3.45 g, 78%): mp 127−130 °C dec; IR (KBr, cm^{-1}) 3121, 3036, 1654, 1587, 1522, 1332, 1262; ^1H NMR ($CDCl_3$; δ, ppm) 8.27 (d, J = 13.8 Hz, 1 H), 8.19−8.10 (m, 2 H), 8.08−7.82 (m, 2 H), 7.78 (d, J = 13.8 Hz, 1 H), 7.21 (s, 1 H); ^{13}C NMR ($CDCl_3$; δ, ppm) 183.9, 182.9, 144.6, 140.3, 138.3, 134.65, 134.67, 132.0, 131.7, 130.9, 127.3, 126.5; CI HRMS m/z (M + H) calcd 230.0453, found 230.0454. Anal. Calcd for $C_{12}H_7NO_4$: C, 62.89; H, 3.08; N, 6.11. Found: C, 63.03; H, 3.05; N, 6.14.

[(±)−(2α,3α,9aα)]-1,2,3,9a-Tetrahydro-2β-ethoxy-3β-nitroanthraquinone (5e). Compound **1b** (0.200 g, 0.873 mmol) was dissolved in THF (5 mL) and cooled to 0 °C, and ethyl vinyl ether (0.10 mL, 1.05 mmol) was added, with stirring. The solution was stirred at 0 °C for 4 h, and then the solvent was evaporated under vacuum, giving **5e** as a light brown solid (0.230 g, 87%). An analytical sample was prepared in a separate experiment as above, except that the reaction solution was stirred at room temperature for 1 h, and then hexane (10 mL) was added, causing **5e** to precipitate. The mixture was cooled at 0 °C for 10 min and then vacuum-filtered, giving **5e** as a light brown microcrystalline solid (0.090 g, 35%): mp 104−106 °C dec; IR (KBr, cm^{-1}) 2995, 1703, 1679, 1590, 1553, 1290; ^1H NMR (acetone-d_6; δ, ppm) (note: this tautomer, **5e,** is unstable in acetone, so spectral data must be collected immediately after it is dissolved in this solvent) 8.22−8.16 (m, 1 H), 8.10−8.04 (m, 1 H), 7.93−7.87 (m, 2 H), 7.02 (dt, J = 3.2, 3.2, 0.3 Hz, 1 H), 5.75 (dt, J = 4.5, 3.3, 3.3 Hz, 1 H), 4.36 (ddd, J = 7.8, 4.5, 2.7 Hz, 1 H), 4.19 (ddt, J = 6.9, 6.0, 3.0, 3.0 Hz, 1 H), 3.74 (dq, J = 9.3, 6.9, 6.9, 6.9 Hz, 1 H), 3.59 (dq, J = 9.3, 6.9, 6.9, 6.9 Hz, 1 H), 2.90 (ddd, J = 14.4, 8.4, 5.4 Hz, 1 H), 2.29 (ddd, J = 14.4, 6.9, 2.4 Hz, 1 H), 1.04 (t, J = 6.9, 6.9 Hz, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 192.7, 185.0, 138.4, 135.3, 134.8, 134.7, 134.4, 127.0, 126.7, 126.0, 82.6, 72.7, 64.4, 46.7, 22.1, 14.4; FAB HRMS m/z (M^+) calcd 301.0950, found 301.0952. Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.80; H, 5.16; N, 4.59.

5,6-Dihydro-6-methoxy-7-nitronaphthalene-1,4-diol (6a). Methyl vinyl ether was prepared from sodium and bromoacetaldehyde dimethyl acetal.[9] Sodium spheres (4.6 g, 0.20 mol) were added to toluene (70 mL), and a solution of bromoacetaldehyde dimethyl acetal (16.9 g, 0.10 mol) in toluene (30 mL) was added dropwise, with vigorous stirring, over 45 min. The resulting methyl vinyl ether gas was bubbled through a solution of **1a** (0.400 g, 2.24 mmol) in THF (4 mL), with stirring, for 45 min. The solvent was evaporated in a stream of N_2, and the resulting residue was crystallized from acetone/H_2O, giving **6a** as a red microcrystalline solid (0.249 g, 47%): mp 219−220 °C dec; IR (KBr, cm^{-1}) 3407, 3212, 1636, 1483, 1384, 1328, 1298, 1268, 1062; ^1H NMR (acetone-d_6; δ, ppm) 8.88 (s, 1 H, exchanges with D_2O), 8.46 (d, J = 0.9 Hz, 1 H), 8.20 (s, 1 H, exchanges with D_2O), 6.94 (d, J = 8.7 Hz, 1 H), 6.75 (dd, J = 8.7, 0.9 Hz, 1 H), 4.86 (m, 1 H), 3.75 (dd, J = 18.3, 1.8 Hz, 1 H), 3.36 (s, 3 H), 2.77 (ddd, J = 18.3, 5.7, 0.9 Hz, 1 H); ^{13}C NMR (acetone-d_6; δ, ppm) 150.3, 147.9, 145.5, 128.9, 121.7, 120.8, 117.3, 114.1, 68.9, 55.8, 27.5; CI HRMS m/z ($M + NH_4^+$) calcd 255.0981, found 255.0987. Anal. Calcd for $C_{11}H_{11}NO_5$: C, 55.69; H, 4.67; 5.91 N. Found: C, 55.80; H, 4.78; N, 5.74.

6-Ethoxy-5,6-dihydro-7-nitronaphthalene-1,4-diol (6b). A. Reaction in Neat Heterocycle. Compound **1a** (0.500 g, 2.79 mmol) was added to ethyl vinyl ether (25 mL), and the mixture was refluxed. A red color developed, and the solid brown starting material was gradually replaced by solid red product. After being refluxed for 3 h, the mixture was cooled to 0 °C and vacuum-filtered and the residue dried under high vacuum, giving **6b** as a red powder (0.375 g, 53%): mp 212 °C dec; IR (KBr, cm^{-1}) 3406, 1633, 1486, 1384, 1326, 1262, 1095, 1052; ^1H NMR (acetone-d_6; δ, ppm) 8.78 (s, 1 H, exchanges with D_2O), 8.42 (s, 1 H), 8.11 (s, 1 H, exchanges with D_2O), 6.91 (d, J = 8.7 Hz, 1 H), 6.73 (d, J = 8.7 Hz, 1 H), 4.93 (d, J = 5.7 Hz, 1 H), 3.73−3.48 (m, 3 H), 2.76 (dd, J = 18.3, 5.7 Hz, 1 H), 1.07 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 150.9, 148.6, 146.5, 129.4, 122.5, 121.4, 118.0, 114.8, 68.1, 64.8, 28.9, 15.7; EI HRMS m/z (M^+) calcd 251.0794, found 251.0800. Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; 5.58 N. Found: C, 57.58; H, 5.10; N, 5.40.

B. Reaction in Benzene. Compound **1a** (0.200 g, 1.12 mmol) and benzene (5 mL) were stirred for 10 min. Then ethyl vinyl ether (89.0 mg, 1.23 mmol) was added, and stirring was continued for 3 h. The solvent was evaporated under vacuum, giving a red solid, which was crystallized from THF/hexane, giving **6b** as a red powder. The filtrate was evaporated and triturated with CH_2Cl_2 (2 mL), giving more **6b,** which was vacuum-filtered (total 0.124 g, 44%): mp 212 °C dec; the ^1H NMR spectrum was identical with that of the red powder obtained in reaction A.

5,6-Dihydro-6-(2-methyl-2-propoxy)-7-nitronaphthalene-1,4-diol (6c) and 2,3-Dihydro-2-(2-methyl-2-propoxy)-4-(2-nitrovinyl)benzo[*b*]furan-5-ol (7c). Compound **1a** (0.200 g, 1.12 mmol) was dissolved in THF (2 mL), *tert*-butyl vinyl ether (0.123 g, 1.23 mmol) was added, and the solution was stirred for 90 min. The THF was evaporated in a stream of N_2, giving an oily red solid, which was separated by flash chromatography (2:1 and then 1:1 hexane/EtOAc), giving two major colored bands.

The solvent containing the first band was evaporated under reduced pressure, and the resulting yellow oily crystals were recrystallized from CH_2Cl_2/cyclohexane, giving **7c** as a yellow microcrystalline solid. An analytical sample was prepared by an additional recrystallization from CH_2Cl_2/cyclohexane, giving **7c** as yellow needles (0.050 g, 16%): mp 167−170 °C; IR (KBr, cm^{-1}) 3387, 2977, 1630, 1594, 1508, 1452, 1330, 1266, 1242, 954; ^1H NMR ($CDCl_3$; δ, ppm) 7.98 (d, J = 13.8 Hz, 1 H), 7.90 (d, J = 13.8 Hz, 1 H), 6.74 (d, J = 8.7 Hz, 1 H), 6.58 (d, J = 8.7 Hz, 1 H), 6.08 (dd, J = 6.7, 2.5 Hz, 1 H), 5.97 (br s, 1 H), 3.46 (dd, J = 16.8, 6.6 Hz, 1 H), 3.14 (dd, J = 16.8, 2.5 Hz, 1 H), 1.37 (s, 9 H); ^{13}C NMR ($CDCl_3$; δ, ppm) 152.3, 150.8, 139.5, 132.9, 128.4, 115.4, 115.0, 113.7, 101.5, 76.5, 38.3, 28.9, 27.1; EI HRMS m/z (M^+) calcd 279.1107, found 279.1095. Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.20; H, 6.14; 5.02 N. Found: C, 60.16; H, 6.06; N, 4.90.

The solvent containing the second band was evaporated under vacuum, and the dark orange residue was recrystallized from THF/cyclohexane, giving **6c** as a yellow solid (0.116 g, 37%): mp 210 °C dec (sealed tube); IR (KBr, cm^{-1}) 3448, 3223, 2977, 1630, 1492, 1458, 1384, 1321, 1273, 1174, 1090; ^1H NMR (acetone-d_6; δ, ppm) 8.75 (br s, 1 H), 8.38 (s, 1 H), 8.08 (br s, 1 H), 6.92 (d, J = 8.7 Hz, 1 H), 6.74 (dd, J = 8.7, 0.7 Hz, 1 H), 5.24 (m, 1 H), 3.68 (dd, J = 18.0, 1.8 Hz, 1 H), 2.78 (dd, J = 18.0, 4.6 Hz, 1 H), 1.26 (s, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 150.0, 148.0, 147.4, 128.4, 122.0, 120.4, 117.5, 113.9, 74.3, 61.0, 31.3, 28.5; EI HRMS m/z (M^+) calcd 279.1107, found 279.1107. Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.20; H, 6.14; 5.02 N. Found: C, 60.13; H, 6.16; N, 5.04.

1,2-Dihydro-2-ethoxy-3-nitroanthracene-9,10-diol (6e). Compound **1b** (0.200 g, 0.873 mmol) and ethyl vinyl ether (5 mL) were heated at reflux for 2 h, with stirring. The resulting mixture was cooled to 0 °C and filtered, giving **6e** as a red solid. An analytical sample was prepared by recrystallization with CH_2Cl_2, giving a red powder (0.110 g, 42%): mp 105 °C dec; IR (KBr, cm^{-1}) 3448, 3101, 1669, 1658, 1624, 1585, 1532, 1502, 1333, 1302, 1194, 1082, 705; ^1H NMR (acetone-d_6; δ, ppm) 9.19 (s, 1 H), 8.74 (d, J = 0.9 Hz, 1 H), 8.36 (d, J = 7.2 Hz, 1 H), 8.28 (d, J = 7.2 Hz, 1 H), 8.03 (s, 1 H), 7.65 (ddd, J = 8.7, 7.2, 1.5 Hz, 1 H), 7.57 (ddd, J = 8.7, 7.2, 1.5 Hz, 1 H), 5.04 (ddd, J = 4.8, 1.8, 0.9 Hz, 1 H), 3.96 (dd, J = 17.4, 1.8

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Hz, 1 H), 3.73 (dq, J = 9.0, 7.2, 7.2, 7.2 Hz, 1 H), 3.58 (dq, J = 9.0, 7.2, 7.2, 7.2 Hz, 1 H), 2.93 (dd, J = 17.4, 4.8 Hz, 1 H), 1.09 (td, J = 7.2, 7.2, 1.8 Hz, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 169.2, 158.5, 148.1, 145.9, 142.7, 136.6, 129.2, 127.9, 125.6, 122.9, 122.1, 113.8, 67.5, 64.1, 28.3, 14.9; FAB HRMS m/z (M^+) calcd 301.0950, found 301.0957. Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.89; H, 4.88; N, 4.75.

2,3-Dihydro-2-methoxy-2-methyl-4-(2-nitrovinyl)benzo[*b*]furan-5-ol (7d). Compound **1a** (0.200 g, 1.12 mmol) was dissolved in THF (2 mL), and 2-methoxypropene (0.320 g, 4.44 mmol) was added, with stirring. After 30 min, solvent was removed under vacuum, giving a red glass. Addition of 1,2-dichloroethane (2 mL) dissolved the glass and caused precipitation of **7d** as a bright yellow powder, which was vacuum-filtered and dried under high vacuum (0.092 g, 33%): mp 194−196 °C; IR (KBr, cm^{-1}) 3300, 1630, 1596, 1503, 1450, 1385, 1336, 1276, 1034, 834; ^{1}H NMR (acetone-d_6; δ, ppm) 9.27 (s, 1H), 8.10 (d, J = 13.8 Hz, 1 H), 7.98 (d, J = 13.8 Hz, 1 H), 6.83 (d, J = 8.7 Hz, 1 H), 6.79 (d, J = 8.7 Hz, 1 H), 3.45 (d, J = 17.4 Hz, 1 H), 3.37 (d, J = 17.4 Hz, 1 H), 3.26 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 152.3, 151.9, 138.9, 132.5, 128.8, 115.0, 114.3, 113.2, 111.8, 49.0, 40.6, 23.5; FAB HRMS m/z (M^+) calcd 251.0794, found 251.0798. Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.50; H, 5.03; N, 5.43.

2-Methyl-4-(2-nitrovinyl)benzo[*b*]furan-5-ol (8d). Compound **1a** (0.200 g, 1.12 mmol) was dissolved in THF (2 mL), and 2-methoxypropene (0.089 g, 1.23 mmol) was added, with stirring. After 5.5 h, the THF was evaporated under vacuum, giving a red solid. The solid was mixed with benzene (3 mL), a catalytic amount of TsOH·H_2O (1 mg, 5 μmol) was added, with stirring, and the mixture was refluxed for 2.5 h. The benzene was evaporated under vacuum, and the red residue was dissolved in hot $CHCl_3$ and filtered hot. Concentration and cooling gave **8d** as maroon microcrystals, which were vacuum-filtered. The filtrate was eluted with $CHCl_3$ through a plug of silica gel, and the resulting solid was crystallized similarly, giving additional **8d** (total 0.093 g, 53%): mp 175−178 °C; IR (KBr, cm^{-1}) 3396, 1610, 1438, 1330, 1267, 1254; ^{1}H NMR (acetone-d_6; δ, ppm) 9.64 (br s, 1 H), 8.41 (d, J = 13.5 Hz, 1 H), 8.12 (d, J = 13.5 Hz, 1 H), 7.44 (dd, J = 8.7, 0.6 Hz, 1 H), 6.93 (d, J = 8.7 Hz, 1 H), 6.88 (q, J = 0.9 Hz, 1 H), 2.49 (d, J = 0.9 Hz, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 158.7, 155.0, 149.0, 138.0, 132.7, 131.1, 115.2, 111.7, 108.3, 102.6, 13.4; EI HRMS m/z (M^+) calcd 219.0532, found 219.0530. Anal. Calcd for $C_{11}H_9NO_4$: C, 60.28; H, 4.14; N, 6.39. Found: C, 60.01; H, 4.36; N, 6.17.

2-Nitroanthraquinone (9). A solution of **5e** (0.220 g, 0.733 mmol) in EtOH (10 mL) was refluxed for 1 h, during which a red color developed. The solution was cooled to room temperature and kept for 12 h. The EtOH was evaporated under vacuum, giving a tan residue. Flash chromatography on silica gel (CH_2Cl_2) gave **9** as a pale yellow solid (0.055 g, 25%): mp 185−186 °C (lit.[10b,c] mp 185−186 °C, 183−184 °C). The experimental IR spectrum agrees with published data.[10a] IR (KBr, cm^{-1}) 3067, 1681, 1595, 1524, 1327, 1296; ^{1}H NMR ($CDCl_3$: δ, ppm) 9.11 (d, J = 2.1 Hz, 1H), 8.61 (dd, J = 8.4, 2.1 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.45=8.37 (m, 2H), 7.93−7.84 (m, 2H); ^{13}C NMR ($CDCl_3$; δ, ppm) 180.1, 179.6, 149.8, 135.5, 133.5, 133.2, 131.8, 131.7, 127.8, 126.6, 126.3, 126.25, 121.2; EI HRMS m/z (M^+) calcd 253.0375, found 253.0377. Anal. Calcd for $C_{14}H_7NO_4$: C, 66.41; H, 2.79; N, 5.53. Found: C, 66.22; H, 2.60; N, 5.44.

(±)-2,3,3aα,4β,9aβ,9bα-Hexahydro-3aα-methoxy-4α-nitro-1*H*-cyclopenta[*a*]naphthalene-6,9-dione (11a) and cis-2,3,3a,8b-Tetrahydro-3a-methoxy-8-(2-nitrovinyl)-1*H*-cyclopenta[*b*]benzofuran-7-ol (13a). Compound **1a** (0.400 g, 2.23 mmol) was mixed with benzene (10 mL) for 10 min, and 1-methoxycyclohexene (0.241 g, 2.45 mmol) was added, with stirring. A red solution formed along with a yellow precipitate. After 3 h, this precipitate was vacuum-filtered and purified by flash chromatography on silica gel (3:1 hexane/EtOAc), giving **13a** as a yellow solid (0.208 g, 34%): mp 170−174 °C dec; IR (KBr, cm^{-1}) 3271, 2951, 1636, 1592, 1516, 1445, 1336, 1279, 1226, 1072, 820; ^{1}H NMR ($CDCl_3$; δ, ppm) 8.08 (d, J = 13.5 Hz, 1 H), 8.02 (d, J = 13.5 Hz, 1 H), 6.79 (d, J = 8.7 Hz, 1 H), 6.65 (d, J = 8.7 Hz, 1 H), 5.41 (br s, 1 H), 3.74 (dd, J = 9.6, 3.0 Hz, 1 H), 3.39 (s, 3 H), 2.42−2.24 (m, 2 H), 2.04 (ddd, J = 12.9, 11.1, 6.6 Hz, 1 H), 1.87−1.62 (m, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 152.9, 152.8, 139.4, 133.0, 132.3, 124.4, 115.7, 113.9, 113.0, 50.8, 48.7, 37.7, 33.2, 24.1; EI HRMS m/z (M^+) calcd 277.0950, found 277.0950. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; 5.05 N. Found: C, 60.46; H, 5.59; N, 4.98.

The original filtrate was evaporated to a red residue, which was triturated with CH_2Cl_2 (2 mL) and vacuum-filtered, giving **11a** as a dark yellow powder (0.034 g, 5%): mp 110−111 °C dec; IR (KBr, cm^{-1}) 2966, 1702, 1638, 1554, 1498, 1458, 1337, 1266, 1219, 1103, 823; ^{1}H NMR ($CDCl_3$; δ, ppm) 6.94 (d, J = 10.5 Hz, 1 H), 6.91 (d, J = 10.5 Hz, 1 H), 6.86 (dd, J = 4.5, 3.3 Hz, 1 H), 5.46 (dd, J = 4.5, 2.1 Hz, 1 H), 3.31 (ddd, J = 6.9, 3.0, 2.4 Hz, 1 H), 3.27 (s, 3 H), 3.01 (tdd, J = 6.9, 6.9, 4.2, 1.5 Hz, 1 H), 2.38−2.26 (m, 1 H), 2.19 (dtd, J = 14.1, 6.6, 6.6, 1.5 Hz, 1 H), 1.80 (ddd, J = 14.1, 7.5, 5.7 Hz, 2 H), 1.67−1.52 (m, 2 H); ^{13}C NMR (the compound was too insoluble in compatible solvents); FAB HRMS m/z (M^+) calcd 277.0950, found 277.0926. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.55; H, 5.24; N, 5.10.

cis-2,3,3a,9b-Tetrahydro-3a-methoxy-4-nitro-1*H*-cyclopenta[*a*]naphthalene-6,9-diol (12a) and cis-2,3,3a,8b-Tetrahydro-3a-methoxy-8-(2-nitrovinyl)-1*H*-benzo[*b*]cyclopenta[*d*]furan-7-ol (13a). Compound **1a** (0.500 g, 2.79 mmol) was mixed with benzene (12.5 mL) for 10 min, and 1-methoxycyclopentene (0.30 g, 3.1 mmol) was added, with stirring. A yellow precipitate formed after 4.5 h, which was vacuum-filtered and crystallized from CH_2Cl_2, giving **13a** as a yellow powder (0.347 g, 45%): mp 170−174 °C; the ^{1}H NMR spectrum was identical with that of **13a** prepared as described above.

The original filtrate was concentrated to 2 mL, and THF (15 mL) and a 10% solution of Et_3N in THF (0.2 mL) were added, with stirring, causing an immediate color change to dark red. After 15 min, the THF was evaporated under vacuum, giving a red oil, which solidified. This solid was treated with activated carbon in acetone and filtered and the acetone evaporated, giving a red solid. Trituration of this solid with $CHCl_3$ gave **12a** as a fine red-orange powder (0.159 g, 21%): mp 209−210 °C dec; IR (KBr, cm^{-1}) 3424, 3272, 2940, 1628, 1493, 1310, 1270, 1059, 815; ^{1}H NMR (acetone-d_6; δ, ppm) 8.80 (br s, 1 H), 8.56 (s, 1 H), 8.19 (br s, 1 H), 6.92 (d, J = 8.7 Hz, 1 H), 6.74 (d, J = 8.7 Hz, 1 H), 3.52 (dd, J = 12.0, 6.6 Hz, 1 H), 2.87 (s, 3 H), 2.65−2.48 (m, 2 H), 2.25−2.04 (m, 1 H), 1.80−1.56 (m, 2 H) 1.14 (qd, J = 12.3, 12.3, 12.3, 6.3 Hz, 1 H); ^{13}C NMR (acetone-d_6; δ, ppm) 149.8, 146.4, 144.9, 128.9, 127.0, 120.4, 115.3, 113.8, 81.4, 50.4, 47.9, 41.3, 35.2, 22.6; FAB HRMS m/z (M^+) calcd 277.0950, found 277.0972. Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.45; H, 5.24; N, 4.92.

(±)-4aα,4bβ,5,6,7,8,8aβ,9α-Octahydro-8aβ-methoxy-9β-nitrophenanthrene-1,4-dione (11b). Compound **1a** (0.200 g, 1.12 mmol) was mixed with benzene (5 mL) for 10 min, and 1-methoxycyclohexane (0.500 g, 4.46 mmol) was added, with stirring. A yellow precipitate developed, and after 24 h was vacuum-filtered and dried under high vacuum, giving **11b** as a yellow powder (0.078 g, 24%). A sample was prepared for X-ray analysis by crystallization from CH_2Cl_2: mp 155−160 °C dec; IR (KBr, cm^{-1}) 2939, 1700, 1640, 1550, 1368, 1272, 1069, 821; ^{1}H NMR (benzene-d_6, 50 °C; δ, ppm) 6.33 (br s, 1 H), 6.10 (d, J = 10.2 Hz, 1 H), 6.01 (d, J = 10.2 Hz, 1 H), 4.58 (dd, J = 4.5, 2.1 Hz, 1 H), 2.93 (m, 1 H), 2.84 (s, 3 H), 2.71 (br

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s, 1 H), 1.52 (m, 1 H), 1.34−0.85 (m, 6 H), 0.40 (s, 1 H); ^{13}C NMR (the compound was too insoluble in compatible solvents); FAB HRMS *m/z* (M + H$^+$) calcd 292.1185, found 292.1163. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; 4.81 N. Found: C, 61.78; H, 5.83; N, 4.76.

(±)-8a*β*-Ethoxy-4aα,4b*β*,5, 6,7,8,8a*β*,9α-octahydro-9*β*-nitrophenanthrene-1,4-dione (11c) and *cis*-5a-Ethoxy-5a,6,7,8,9,9a-hexahydro-1-(2-nitrovinyl)dibenzofuran-2-ol (13c). Compound **1a** (0.400 g, 2.23 mmol) was mixed with benzene (10 mL) for 10 min, and 1-ethoxycyclohexene (0.310 g, 2.46 mmol) was added, with stirring. A precipitate formed after 2 h, and after 18 h the mixture was vacuum-filtered. The precipitate was washed with benzene and vacuum-dried, giving **11c** as a pale yellow powder. The benzene from the combined filtrate and washings was evaporated under vacuum, giving an oil, which crystallized. Addition of EtOAc (2 mL), mixing, and filtering gave yellow crystals, which were recrystallized from CH_2Cl_2, giving additional **11c** (total 0.152 g, 22%): mp 164−166 °C dec; IR (KBr, cm^{-1}) 2935, 1702, 1638, 1550, 1366, 1268, 1097, 821; ^{1}H NMR (benzene-d_6, 50 °C; δ, ppm) 6.32 (br s, 1 H), 6.13 (d, J = 10.2 Hz, 1 H), 6.03 (d, J = 10.2 Hz, 1 H), 4.63 (dd, J = 3.9, 1.8 Hz, 1 H), 3.25−2.91 (m, 3 H), 2.73 (br s, 1 H), 1.70−1.40 (m, 2 H), 1.35−0.70 (brm, 6 H), 0.83 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (the compound was too insoluble in compatible solvents); CI HRMS *m/z* (M + H$^+$) calcd 306.1341, found 306.1342. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.99; H, 6.12; N, 4.52.

The EtOAc filtrate was concentrated and purified by flash chromatography on silica gel (3:1 hexane/EtOAc), giving a mixture of **13c** and the EtOH elimination product **14** (n = 2) in a 3.9:1 ratio. Recrystallization from EtOH/H_2O followed by recrystallization from $CHCl_3$ gave **13c** as yellow needles (0.083 g, 12%): mp 160−162 °C; IR (KBr, cm^{-1}) 2946, 1626, 1509, 1450, 1384, 1334, 1328, 1068, 826; ^{1}H NMR (acetone-d_6; δ, ppm) 9.40 (br s, 1 H), 8.19 (d, J = 13.5 Hz, 1 H), 8.03 (d, J = 13.5 Hz, 1 H), 6.86 (d, J = 8.7 Hz, 1 H), 6.81 (d, J = 8.7 Hz, 1 H), 3.59 (q, J = 6.9 Hz, 2 H), 3.31 (dd, J = 10.8, 6.9 Hz, 1 H), 2.51−2.43 (m, 1 H), 2.30−2.18 (m, 1 H),1.84−1.69 (m, 2 H), 1.60 (dd, J = 8.4, 4.2 Hz, 1 H), 1.48−1.31 (m, 2 H), 1.12−0.99 (m, 1 H), 0.98 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 152.6, 150.6, 139.4, 137.9, 132.4, 114.24, 114.26, 113.9, 110.9, 56.3, 46.7, 31.3, 30.3, 21.9, 21.7, 15.1; EI HRMS *m/z* (M$^+$) calcd 305.1263, found 305.1262. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.07; H, 6.31; N, 4.55.

6,7,8,9-Tetrahydro-1-(2-nitrovinyl)dibenzofuran-2-ol (14d). A. Reaction in Benzene. Compound **1a** (0.200 g, 1.12 mmol) was mixed with benzene (5 mL) for 10 min, and 1-trimethylsiloxycyclohexene (0.210 g, 1.23 mmol) was added, with stirring, causing the color to change to dark red, which lightened to cherry red over several hours. A precipitate formed, which was filtered after 24 h and dried, giving **14d** as a yellow powder (0.159 g, 55%). An analytical sample was obtained by recrystallization from EtOH/H_2O, giving **14d** as an orange microcrystalline solid: mp 195−197 °C; IR (KBr, cm^{-1}) 3382, 2930, 1606, 1493, 1436, 1329, 1262, 1230; ^{1}H NMR (acetone-d_6; δ, ppm) 9.80 (br s, 1 H), 8.48 (d, J = 13.2 Hz, 1 H), 8.22 (d, J = 13.2 Hz, 1 H), 7.40 (d, J = 8.7 Hz, 1 H), 6.90 (d, J = 8.7 Hz, 1 H), 2.90−2.85 (m, 2 H), 2.76−2.72 (m, 2 H), 1.98−1.88 (m, 4 H); ^{13}C NMR (acetone-d_6; δ, ppm) 157.3, 155.1, 148.4, 138.4, 132.5, 128.2, 114.7, 112.9, 111.3, 109.2, 23.4, 22.9, 22.6, 21.9; EI HRMS *m/z* (M$^+$) calcd 259.0844, found 259.0843. Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.87; H, 4.99; N, 5.19.

B. Reaction in THF. Compound **1a** (0.200 g, 1.12 mmol) was dissolved in THF (2 mL), and trimethylsiloxycyclohexene (0.380 g, 2.24 mmol) was added. The solution was stirred at room temperature for 24 h, and then the THF was evaporated under reduced pressure, giving a red oil. The oil was dissolved in MeOH (2 mL), 2 N HCl (0.2 mL) was added, and the solution was stirred for 12 h, during which a precipitate formed. The solution was concentrated to half its original volume and then vacuum-filtered, giving **14d** as a yellow solid in two crops. This was recrystallized from EtOH/H_2O, giving **14d** as an orange solid (0.115 g, 40%): mp 195−197 °C; the ^{1}H NMR spectrum was identical with that of the sample from reaction A.

(±)-6a*β*,7,8,9,10,11,11a*β*,11bα-Octahydro-6a*β*-methoxy-6*β*-nitro-6*H*-cyclohepta[*a*]naphthalene-1,4-dione (11e) and *cis*-5a,7,8,9,10,10a-Hexahydro-5a-methoxy-1-(2-nitrovinyl)-6*H*-benzo[*b*]cyclohepta[*d*]furan-2-ol (13e). Compound **1a** (0.400 g, 2.23 mmol) was mixed with benzene (10 mL) for 10 min, and 1-methoxycycloheptene (0.310 g, 2.46 mmol) was added, with stirring. A precipitate formed within the first hour, and after 18 h the mixture was vacuum-filtered, giving **11e** as a yellow powder (0.146 g, 21%): mp 160−162 °C dec; IR (KBr, cm^{-1}) 3065, 2948, 2922, 2873, 1699, 1641, 1551, 1459, 1368, 1274, 1095, 1069, 824; ^{1}H NMR ($CDCl_3$; δ, ppm) 6.91 (d, J = 10.2 Hz, 1 H), 6.87 (d, J = 10.2 Hz, 1 H), 6.68 (dd, J = 3.9, 3.0 Hz, 1 H), 5.33 (dd, J = 3.9, 2.4 Hz, 1 H), 3.46 (ddd, J = 5.4, 2.7, 2.4 Hz, 1 H), 3.25 (s, 3 H), 3.19 (dddd, J = 8.7, 5.4, 2.4, 0.8 Hz, 1 H), 2.15−2.08 (m, 1 H), 1.96−1.87 (m, 2 H), 1.83−1.56 (m, 6 H), 1.38−1.23 (m, 1 H);^{13}C NMR (the compound was too insoluble in compatible solvents); CI HRMS *m/z* (M + H$^+$) calcd 306.1341, found 306.1342. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.79; H, 6.11; N, 4.42.

The benzene from the original filtrate was evaporated under vacuum. The resulting residue was dissolved in THF (10 mL) and cooled to 0 °C. A catalytic amount of Et_3N (4 μL of a 10% solution in THF) was added, with stirring, causing the color to turn a darker shade of red. After 1 h, the THF was evaporated under vacuum and the red residue was separated by flash chromatography on silica gel (3:1 and then 1:1 hexane/EtOAc), giving **13e** as the first major yellow band. Evaporation of the solvent gave **13e** as a red oil, which crystallized upon standing. An analytical sample was prepared by trituration with hexane (0.340 g, 50%): mp 67−70 °C; IR (KBr, cm^{-1}) 3539, 2928, 2856, 1690, 1628, 1512, 1445, 1343, 1271, 970; ^{1}H NMR ($CDCl_3$; δ, ppm) 9.42 (br s, 1 H), 8.14 (d, J = 13.2 Hz, 1 H), 8.05 (d, J = 13.2 Hz, 1 H), 6.85 (d, J = 8.4 Hz, 1 H), 6.79 (d, J = 8.4 Hz, 1 H), 3.53−3.44 (m, 1 H), 3.23 (s, 3 H), 2.45 (dd, J = 14.7, 8.7 Hz, 1 H), 1.92−1.32 (m, 10 H); ^{13}C NMR (acetone-d_6; δ, ppm) 152.8, 150.8, 139.5, 134.1, 131.9, 116.2, 115.3, 113.9, 113.5, 53.8, 48.3, 31.7, 31.5, 30.5, 29.4, 22.7; FAB HRMS *m/z* (M$^+$) calcd 305.1263, found 305.1264. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.74; H, 6.50; N, 4.28.

(±)-6a*β*,7,8,9,10,11,11a*β*,11bα-Octahydro-6a*β*-methoxy-6*β*-nitro-6*H*-cyclohepta[*a*]naphthalene-1,4-dione (11e) and 7,8,9,10-Tetrahydro-1-(2-nitrovinyl)-6*H*-benzo[*b*]cyclohepta[*d*]furan-2-ol (14e). Compound **1a** (0.400 g, 2.23 mmol) was dissolved in THF (4 mL), and 1-methoxycycloheptene (0.660 g, 3.23 mmol) was added, with stirring. A precipitate formed within 30 min, and after 3 h, the mixture was vacuum-filtered and the precipitate was triturated with CH_2Cl_2 (3 mL), giving **11e** as a yellow powder (0.062 g, 9%): mp 160−162 °C dec; the ^{1}H NMR spectrum was identical with that of **11e** obtained previously.

The THF from the original filtrate was evaporated, and the resulting dark red oil was dissolved in benzene (7.5 mL). TsOH·H_2O (2.0 mg, 0.01 mmol) was added, and the solution was heated at reflux for 30 min, with stirring. The solution was cooled to room temperature, causing crystals to form. Further cooling at 4 °C for 1 h, followed by vacuum-filtration, gave **14e** as yellow crystals. An analytical sample was obtained by recrystallization from $CHCl_3$ (0.255 g, 42%): mp 183−185 °C; IR (KBr, cm^{-1}) 2927, 2852, 1607, 1499, 1430, 1384, 1332, 1264; ^{1}H NMR (acetone-d_6; δ, ppm) 9.73 (s, 1 H), 8.71 (d, J = 13.2 Hz, 1 H), 8.22 (dd, J = 13.2, 1.5 Hz, 1 H), 7.42 (d, J = 8.7 Hz, 1 H), 6.95 (d, J = 8.7 Hz, 1 H), 3.07−2.88 (m, 4 H), 2.10−1.91 (m, 6 H); ^{13}C NMR (acetone-d_6; δ, ppm) 159.7, 155.0, 147.7, 138.6, 132.3, 130.6, 116.8, 114.5, 111.4, 109.1, 28.7, 27.6, 27.1, 25.3, 25.2; EI HRMS *m/z* (M$^+$) calcd 273.1001, found 273.0999. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.87; H, 5.36; N, 4.96.

(±)-4b*β*,5,6,7,8,8a,9α,10*β*-Octahydro-8a*β*,10α-dimethoxy-9*β*-nitrophenanthrene-1,4-diol (15). Compound **11b** (0.067 g, 0.23 mmol) was mixed with MeOH (5 mL) and H_2O (1 drop), and the mixture was heated to reflux. Acetonitrile (2.5 mL) was added to fully dissolve the solid, and refluxing was continued for 30 min. The solvents were evaporated under vacuum, giving a yellow oil, which solidified upon standing. Crystallization from benzene, followed by recrystallization from MeOH/H_2O, gave **15** as pale yellow prisms (0.051 g, 68%): mp 215−220 °C; IR (KBr, cm^{-1}) 3454, 3383, 2932, 1553, 1468, 1257; ^{1}H NMR (500 MHz, acetone-d_6; δ, ppm) 8.02 (s, 1 H), 7.44 (s, 1 H), 6.76 (d, J = 8.5 Hz, 1 H), 6.61 (d, J = 8.5 Hz, 1 H), 5.86 (d, J = 8.5 Hz, 1 H), 5.66 (d, J = 8.5 Hz, 1 H), 3.48 (dd, J = 11.5, 4.5 Hz, 1 H), 3.32 (s, 3 H), 3.00 (s, 3 H), 2.30−2.71 (m, 1 H), 2.07−1.80 (m, 4 H), 1.59−1.41 (m, 3 H); ^{13}C NMR (acetone-d_6; δ, ppm) 149.1, 147.0, 125.7, 118.5, 115.9, 114.1, 86.6, 78.0, 76.0, 52.4, 48.0, 38.0, 30.7, 29.7, 25.2, 22.8; FAB HRMS m/z (M^+) calcd 323.1369, found 323.1378. Anal. Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; 4.33 N. Found: C, 59.60; H, 6.46; N, 4.35.

General Procedure for Conversion of 11 to 12. Compound **11** was dissolved in THF (5 mL per 0.23 mmol of **11**), the solution was cooled to 0 °C, and a 10% solution of Et_3N in THF (1 μL) was added, with stirring, causing the color to change to red. The solution was stirred for 1 h at 0 °C and then allowed to warm to room temperature. The THF was evaporated in a stream of N_2, and the residue was dried under high vacuum. Trituration with CH_2Cl_2 followed by vacuum filtration and drying under high vacuum gave **12** as a yellow to red powder.

***cis*-4b,5,6,7,8,8a-Hexahydro-8a-methoxy-9-nitrophenanthrene-1,4-diol (12b).** Following the general procedure for compound **11b** (0.065 g, 0.22 mmol), **12b** was obtained as a yellow powder (0.048 g, 74%): mp 148−151 °C dec; IR (KBr, cm^{-1}) 3264, 2935, 1623, 1513, 1492, 1326, 1290, 1057; ^{1}H NMR (acetone-d_6; δ, ppm) 8.75 (br s, 1 H), 8.28 (s, 1 H), 8.04 (br s, 1 H), 6.89 (d, J = 8.7 Hz, 1 H), 6.68 (d, J = 8.7 Hz, 1 H), 3.37 (dd, J = 12.6, 4.2 Hz, 1 H), 3.12 (s, 3 H), 3.07 (dm, J = 11.4 Hz, 1 H), 1.97−1.90 (m, 1 H), 1.80 (dd, J = 13.8, 3.0 Hz, 1 H), 1.67−1.56 (m, 1 H), 1.48 (td, J = 13.5, 13.5, 3.3 Hz, 1 H), 1.38 (qt, J = 12.9, 12.9, 12.9, 3.9, 3.9 Hz, 1 H), 1.12−0.87 (m, 2 H); ^{13}C NMR (acetone-d_6; δ, ppm) 148.4, 145.6, 145.0, 129.3, 127.3, 119.4, 114.8, 112.2, 75.0, 49.3, 42.9, 29.8, 29.4, 23.4, 21.8; FAB HRMS m/z (M^+) calcd 291.1107, found 291.1102. Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 62.07; H, 5.95; N, 4.87.

***cis*-8a-Ethoxy-4b,5,6,7,8,8a-hexahydro-9-nitrophenanthrene-1,4-diol (12c).** Following the general procedure for compound **11c** (0.049 g, 0.16 mmol), **12c** was obtained as a yellow-orange powder (0.034 g, 69%): mp 160−161 °C dec; IR (KBr, cm^{-1}) 3260, 2941, 1618, 1508, 1491, 1319, 1284, 1254, 1055; ^{1}H NMR (acetone-d_6; δ, ppm) 8.73 (s, 1 H), 8.26 (s, 1 H), 8.05 (s, 1 H), 6.88 (d, J = 8.7 Hz, 1 H), 6.68 (d, J = 8.7 Hz, 1 H), 3.52 (dq, J = 8.7, 6.9, 6.9, 6.9 Hz, 1 H), 3.39 (dd, J = 12.6, 4.2 Hz, 1 H), 3.22 (dq, J = 8.7, 6.9, 6.9, 6.9 Hz, 1 H), 3.04 (dddd, J = 13.2, 4.2, 2.7, 1.5 Hz, 1 H), 1.91 (dm, J = 13.5 Hz, 1 H), 1.75 (dm, J = 13.5 Hz, 1 H), 1.67−1.55 (m, 1 H), 1.52 (td, J = 14.1, 14.1, 3.3 Hz, 1 H), 1.38 (qt, J = 13.2, 13.2, 13.2, 3.9, 3.9 Hz, 1 H), 1.15−0.90 (m, 2 H), 0.92 (t, J = 6.9, 6.9 Hz, 1 H); ^{13}C NMR (acetone-d_6; δ, ppm) 149.7, 147.3, 146.3, 130.5, 128.9, 120.7, 116.2, 113.5, 76.0, 58.5, 44.4, 32.0, 30.9, 24.8, 23.2, 15.4; EI HRMS m/z (M^+) calcd 305.1263, found 305.1263. Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.02; H, 6.41; N, 4.36.

***cis*-6a,8,9,10,11,11a-Hexahydro-6a-methoxy-6-nitro-7*H*-cyclohepta[*a*]naphthalene-1,4-diol (12e).** Following the general procedure for compound **11e** (0.060 g, 0.20 mmol), **12e** was obtained as a yellow powder (0.043 g, 70%): mp 125−126 °C dec; IR (KBr, cm^{-1}) 3376, 2932, 1626, 1501, 1491, 1455, 1384, 1324, 1279, 1057; ^{1}H NMR (acetone-d_6; δ, ppm) 8.70 (br s, 1 H), 8.22 (br s, 1 H), 8.18 (s, 1 H), 6.91 (d, J = 8.7, 1 H), 6.69 (d, J = 8.7, 1 H), 3.55 (dd, J = 12.0, 2.4 Hz, 1 H), 3.06 (s, 3H), 2.64 (dd, J = 14.1, 9.0 Hz, 1 H), 1.90−1.38 (m, 9 H); ^{13}C NMR (acetone-d_6; δ, ppm) 149.1, 147.7, 146.1, 130.4, 129.3, 120.4, 115.8, 113.5, 79.0, 51.1, 46.6, 33.8, 31.4, 30.0, 29.7, 21.7; FAB HRMS m/z (M^+) calcd 305.1263, found 305.1237.

6,7,8,9-Tetrahydro-1-(2-nitrovinyl)dibenzofuran-2-ol (14c) from 13c. Compound **13c** (10.0 mg, 0.033 mmol) was dissolved in THF (1 mL), TsOH·H_2O (0.6 mg, 3.3 μmol) was added as a 1% (wt) solution in THF, and the solution was refluxed for 1 h, with stirring. The solution was cooled to room temperature, and the THF was evaporated in a stream of N_2. The residue was eluted through a short plug of silica gel (1:1 hexane/EtOAc), and the resulting solid was crystallized from EtOH/H_2O, giving **14c** as an orange microcrystalline solid (6.0 mg, 71%): mp 195−196 °C; the ^{1}H NMR spectrum was identical with that of **14d** prepared as described above.

7,8,9,10-Tetrahydro-1-(2-nitrovinyl)-6*H*-benzo[*b*]cyclohepta[*d*]furan-2-ol (14e) from 13e. Compound **13e** (30.0 mg, 0.098 mmol) was dissolved in THF (3 mL), TsOH·H_2O (5.6 mg, 0.029 mmol) was added, and the solution was refluxed for 15 h, with stirring. The solution was cooled to room temperature, and the THF was evaporated in a stream of N_2. The residue was purified by flash chromatography on silica gel (3:1 hexane/EtOAc), giving **14e** as a yellow powder (23.7 mg, 88%): mp of material recrystallized from $CHCl_3$, 183−185 °C; the ^{1}H NMR spectrum was identical with that of **14e** prepared as described above.

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Supporting Information Available: X-ray structure data for **11b** and ^{1}H NMR data for **12e**. This material is available via the Internet at http://pubs.acs.org.

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